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Dissertation entitled

**Sizing and Optimization of In-Situ Electrolysis Process Generator
of Sodium Hypochlorite for Drinking Water Treatment Plant of
the TICHY-HAF Dam**

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Abstract

Microorganisms and harmful substances that pose a threat to human life represent one of the major problems in water treatment plants, the dissertation provide the details about the different factors and parameters that affect the disinfection process and the production of sodium hypochlorite are provided. The objective of this Dissertation is to design and optimise of the in-situ electrolysis process generator of sodium hypochlorite for drinking water treatment plant of the TICHY-HAF dam.

Keywords: electrolysis, disinfection, on site generation, sodium hypochlorite, optimization, sizing, design, water treatment.

ملخص

تمثل الكائنات الدقيقة والمواد الضارة التي تشكل تهديداً على حياة الإنسان إحدى المشاكل الرئيسية في محطات معالجة المياه، في هذا العمل يتم توفير تفاصيل حول العوامل والإعدادات التي تؤثر على عملية التطهير وإنتاج هيبوكلوريت الصوديوم. الهدف من هذه المذكرة هو القيام بتحسين وتصميم للمصنع الذي تتم فيه عملية إنتاج هيبوكلوريت الصوديوم باستعمال عملية التحليل الكهربائي، لصالح محطة معالجة المياه في سد تيشي حاف.

الكلمات مفتاحية: التحليل الكهربائي، تطهير، توليد في الموقع، هيبوكلوريت الصوديوم، تحسين، تصميم، معالجة المياه.

Résumé

Les micro-organismes et les substances nocives qui menacent la vie humaine représentent l'un des problèmes majeurs dans les stations de traitement des eaux. Des détails sur les différents facteurs et paramètres qui affectent le processus de désinfection et la production d'hypochlorite de sodium sont mentionnés. L'objectif de cette mémoire est d'optimiser et dimensionner un in situ générateur d'hypochlorite de sodium par procédé d'électrolyse, pour la station de traitement des eaux potable du TICHY-HAF barrage.

Mots clés: électrolyse, désinfection, Génération sur site, hypochlorite de sodium, dimensionnement, optimisation, design, traitement des eaux.

Dedication

This Work is dedicated to my beloved parents who never stopped praying for me, supporting me and helping me so that I can achieve my goals. I love you.

To my big brothers YAHIA and SAMIR for helping and supporting me all the time.

To my dear and my only sister IHCENE.

To my family.

To all my friends and colleagues all by their names

And to group 'Zoomiste'.

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List of Abbreviations

UF	Ultrafiltration
NF	Nanofiltration
DNA	Deoxyribonucleic Acid
WHO	World Health Organization
NTU	Nephelometric Turbidity Units
Ct	Exposure Value or Contact time
DBP	Disinfectant By Product
THMs	trihalomethanes
HAAs	Haloacetic Acids
NOM	Naturally Organic Materials
pH	Potential of Hydrogen
GAC	Granular Activated Carbon
DSA	Dimensionally Stable Anode
OSG	On Site Generation
DC	direct current
AC	Available Chlorine
SAC	Strong Acid Cation
ECE	Energy Conversion Efficiencies
TH	Total water Hardness
LEL	Lower Explosive Limit

INTRODUCTION

Introduction

With increasing in the rate of demographic growth in Algeria, and the increasing consumption of drinking water, a shortage of water levels has followed in some areas, especially those dependent on non-renewable wells as a source of water. This has led to an increased reliance on other sources such as dams, which contain varying proportions of soluble and insoluble materials, toxic substances, and microorganisms that may cause illness or even death when consumed by humans. This requires treatment of this water and make it in a state from which infection is not possible. This means that the majority of microorganisms must be destroyed, and inactivated by using some disinfectants like sodium hypochlorite.

Chlorination usage as a disinfectant agent is widely spread especially with the development of sodium hypochlorite production using electrolysis method. However, several questions arise regarding the effectiveness of sodium hypochlorite, and the electrolysis method:

- What are the factors that affect the disinfection process?
- What is the best electrolyzer technology for water treatment?
- What are the parameters that affect the production of sodium hypochlorite using this method?

This work attempts to provide answers to the raised questions, which will help to achieve the main objective of this work is Sizing and Optimization of In-Situ Electrolysis Process Generator of Sodium Hypochlorite for Drinking Water Treatment Plant of the TICHY-HAF Dam.

The first chapter is a general overview of the technologies and methods that is used in the water treatment plant, and the factors that affect the chlorination process.

The second chapter describes the process of the electrolyzer technology that is used in the TICHY-HAF dam, with details about the parameters that affects the production in the seeks of optimizing the process.

The third chapter provides a full design with a sizing for the process.

CHAPTER 1
AN INTRODUCTION TO WATER
TREATMENT

Chapter 1: An Introduction to Water Treatment

1.1-Background

“And We have made of water everything living” (Holy Quran; 21:30). Beside of considering water as the sign of life for every living organism, water play a big role in the daily human life like cleaning, cooking, sanitation, agriculture, industry, and transportation. which make it the most precious matter for every civilisation through history.

Although 71% of earth's surface is covered with water, most of it is saltwater in the oceans to let only 3%, with 2.5% is unavailable that locked up in glaciers, polar ice caps, atmosphere, and soil; highly polluted; or lies too far under the earth's surface to be extracted [1]. And with the huge consummation of water, the rapid growth of population, climate changes and the small amount of fresh water, every country puts water resources as first priority. by protecting their water sources and by possessing the water treatment technology to provide all the water needs, especially drinking water.

At the same time that humans were learning to exert some control over the quantity of water available to them, they found different waters varied in qualities such as temperature, color, taste, and odor. They noted that these qualities influenced the suitability of water for certain purposes. Salty water was not suitable for human and livestock consumption or irrigation. Clear water was superior over turbid water for domestic use. Some waters could cause illness or even death when consumed by humans [2]. Like toxic substances, they are poisonous and cause adverse health effects in both man and animals [3]. Or microorganism's infection diseases, the most common and widespread health risk associated with drinking-water are caused by pathogenic bacteria, viruses and parasites (e.g., protozoa and helminths) [4].

And so, it is necessary to reduce harmful substances and micro-organism using water treatment technologies to eliminate any contamination source, and enhance the water quality.

1.2-Water Treatment Technology

The amount and type of treatment applied by a given public water system will vary depending upon the source type and quality. Many, if not most, groundwater systems can provide adequate treatment that involves little or no treatment of the source. Surface waters, however, are exposed to the atmosphere and surface runoff and are more likely to contain contaminants. Surface water systems, therefore, must implement a greater level of treatment to provide safe and potable drinking water [5].

A variety of water treatment technologies are needed in the treatment plant in order to enhance water quality. One of the main methods used is the cascade aerators which increase the oxidation of iron and manganese by increasing the contact with air, taste and odor control, and removal of volatile compounds. Then there are the coagulation and flocculation methods, which are used for aggregating suspended solids into larger particles to become more filterable. To put it simply coagulation is the addition of chemicals like aluminum sulfate, and ferric sulfate to water to destroy or reduce repulsive forces and induce particle agglomeration. Flocculation is the physical process of promoting particle contact to facilitate the agglomeration to larger settleable floc [6]. Followed by injection of activated carbon in granular or powder form for the removal of organic compounds including compounds producing taste and odors, pesticides, and other synthetic organic compounds. The next step is sedimentation in this step a majority of the settleable solids are removed by gravitational settling, next is the membrane filtration technology, membrane separation processes use semipermeable membranes to separate impurities from water. The membranes are selectively permeable to water and certain solutes. A driving force is used to force the water to pass through the membrane, leaving the impurities behind as a concentrate [5]. Ultrafiltration (UF) and nanofiltration (NF) are highly used in water treatment plants due to their efficiency in removing impurities, especially in a combined UF/NF process. Results showed that UF guaranteed the inlet water quality of NF and NF could efficiently reject organics and salts, with a chloride removal over 95 % [7].

There are other methods like the ion exchange technology that has been used in the chemical and environmental engineering fields for a long time. However, its use has been mostly limited to water softening (Ca^{2+} and Mg^{2+} removal) [8].

Next step in the treatment process is disinfection, which is a necessary step in every water treatment plants.

1.3-Disinfection

Disinfection of drinking water is designed to bring the water into a state from which infection is not possible. This means that the majority of microorganisms must be inactivated. Chemicals allowed to be added to drinking water are the active chlorine species, e.g., dissolved chlorine, hypochlorous acid and hypochlorite ions, furthermore, ozone and chlorine dioxide. The situation is complicated by the fact that chloramines are forbidden in many European countries but are allowed to be added in USA. [9]. Although other alternatives emerged such as ozone, chlorine remains widely used, as the process has proved its efficiency at low price and simple technology. It ensures a high demand for human consumption while complying with microbiological criteria and sustains the necessary residual chlorine to maintain water quality during distribution [10].

Chick's law (1908) expresses the rate of destruction of microorganisms as follow [5]:

$$\ln(N/N_0) = -kC^nT \quad (1.1)$$

where N_0 = the initial concentration of bacteria, N = the concentration of surviving bacteria at time T , k = rate constant (coefficient of specific lethality), C = concentration of the disinfectant, and n = concentration of the dilution. N and N_0 are determined by faecal coliform tests and k is determined from the plot of N_t and N_0 . It is recommended for adequate reaction time and penetration of total suspended solids, that a detention time of between 30 and 45 minutes [5, 6].

1.3.1-Chlorination

The first use of chlorine for disinfection dates back to (1823), when it was used in hospitals. Chlorine water was employed in obstetric wards to prevent puerperal fever in (1826), and fumigation with chlorine was practiced during the great European cholera epidemic. Between (1920) and (1940), several new applications for chlorine were developed, for example, in the manufacture of ethylene glycol, chlorinated solvents, and vinyl chloride [3].

Chlorine can be applied by drinking water treatment plants as chlorine gas, sodium hypochlorite solutions, or as solid calcium hypochlorite. All three forms of chlorine

application are chemically equivalent due to the rapid equilibrium between each of the forms when they are injected into water [11, 5].

When any form of chlorine added to water, a new species forms, known as available chlorine or free chlorine (Cl_2 , HOCl , and OCl^-), those species are not combined with ammonia or organic nitrogen [12]. The relative concentrations of hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) are dependent on the pH and the temperature, the following equations and figure 1.1 show the new species form [5, 13]:

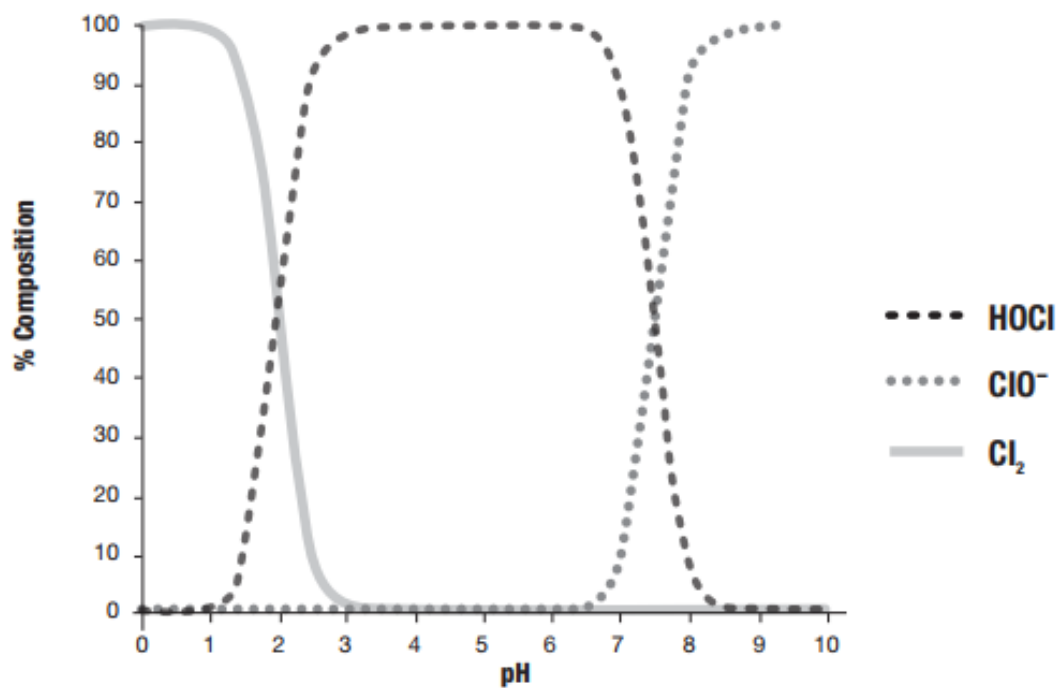


Figure 1.1: Relation between solution pH and chlorine speciation [13].

Both hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-) are strong oxidizing agents. HOCl and OCl^- have been reported to react with a wide variety of biological molecules such as proteins, amino acids, peptides, lipids, and Deoxyribonucleic acid (DNA). It is believed that the mechanism of the germicidal activity of HOCl or OCl^- is due to the inhibition of enzyme activity essential for the growth, damage to the membrane and DNA,

and perhaps an injury to membrane transport capacity although it has not been fully elucidated. HOCl stress is also suggested to generate common deleterious oxidative species which can damage cellular components. At present, sodium hypochlorite (NaOCl) is the most widely used disinfectant in the food industry. Due to its advantages which is represented in a reasonable persistence on treated potable water, rapid bacteria action, relative nontoxicity to humans at use concentrations. colorless, nonflammability, and low cost [14]. Furthermore, the cost and the risk of transportation and storage (chlorine gas) is reduced due to the spreading of on-site sodium hypochlorite technology in water treatment plants.

1.3.2-Factors That Affect the Disinfection Efficiency

The effectiveness of disinfection using chlorination is affected by many variables like the concentration of the disinfectant, degree of pollution, the amount of microorganism and its innate resistance. And beside those variables, there are other factors should be taken into consideration when using disinfectant like the following factors:

1.3.2.1-The Stage at Which Chlorine is Applied

Chlorination can be applied at a number of different points along the water treatment process. Pre-chlorination is used before coagulation-sedimentation or filtration to reduce pathogen levels, to inhibit biofilm or algal development within the plant, and to oxidize any inorganic compounds (e.g., iron and manganese) before the main treatment steps. While post-chlorination is used for disinfection of the finished water as it enters the distribution system [15].

1.3.2.2-Time of Contact

Chlorine disinfection is not an immediate process, and sufficient time must be allowed for chlorine to kill micro-organisms like shown in (section 1.3).

Disinfection phenomena have often been considered as chemical reactions. Consequently, species transport and subsequent residence time in a disinfection tank is of critical importance. A proper disinfection tank design has to ensure a suitable contact time in order to inactivate most of the micro-organisms without the formation of by-products.

Several investigations have been carried out to evaluate the adequate reaction time. More details about chlorine contact evaluation, contact tank design may found in [10].

1.3.2.3-Physical and Chemical Factors

Several physical and chemical factors also influence disinfectant procedures: Temperature, pH, and Water Hardness. For example, the activity of most disinfectants increases as the temperature increases, but some exceptions exist. Furthermore, too great an increase in temperature causes the disinfectant to degrade and weakens its germicidal activity and thus might produce a potential health hazard. While the pH influences the antimicrobial activity by altering the disinfectant molecule or the cell surface, which improves the antimicrobial activity of some and decrease it for others [16]; For example, the effect of pH on sodium hypochlorite when dissolved in water like shown on (Figure 1.1) The guide value suggested by the World Health Organization (WHO) is pH less than 8 [17].

Water hardness (i.e., high concentration of divalent cations) reduces the rate of kill of certain disinfectants because divalent cations (e.g., magnesium, calcium) in the hard water interact with the disinfectant to form insoluble precipitates [16].

1.3.2.4-Effect of Turbidity

The effect of turbidity in a water is to hinder the penetration of chlorine: bacteria can be shielded in particles of suspended matter and thus be protected from the effect of the chlorine. It is always necessary therefore, that final disinfection by chlorine is applied as a final stage of treatment in water which contains low turbidity. For effective disinfection, WHO suggests a guide level value for turbidity of less than 1 Nephelometric Turbidity Units (NTU) [17].

1.3.2.5-The Number of Coliforms

To be confident of achieving 100% compliance with the requirement of zero coliforms after the disinfection stage, the water subjected to disinfection ideally should not contain more than 100 coliforms/100 ml. Most groundwaters satisfy this criterion. In surface waters, coagulation followed by solid-liquid separation processes, achieves up to 99.9% bacteria removal. Consequently, pre-disinfection in addition to conventional treatment is only required for heavily polluted surface waters [17].

1.3.2.6-Exposure Value

Given adequate chlorine concentration and contact time, all bacterial organisms and most viruses can be inactivated. Thus, a useful design criterion for the disinfection process is the product of contact time in (minutes) and the free chlorine residual (the amount of free chlorine remaining after the disinfection.) concentration in (mg/l) at the end of that contact time. This is known as the 'Ct value' or 'exposure value'. On this basis the guide level of 0.5 mg/l free residual concentration after 30 minutes contact proposed by WHO would have a Ct value of 15 (mg.min/l). The WHO Ct criterion of 15 mg.min/l is for faecally polluted water and therefore may be varied according to the bacteriological quality of the source water [17].

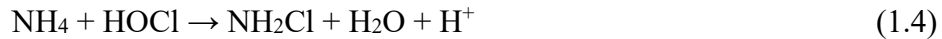
1.3.3-Disinfectant by Products

Chlorine also reacts with natural organic compounds, such as humic matter to produce carcinogenic species which unfortunately cannot be totally removed prior to disinfection even with the latest technologies. These chemical reactions produce more than 250 different disinfection by-products (DBP), while other studies report more than 600 species in drinking water, among which are the trihalomethanes (THMs) such as chloroform, haloacetic acids (HAAs) such as chloroacetic acid. THMs and HAAs received much attention due to their relatively high concentration, although compounds with smaller concentrations might present a higher risk to human health. DBPs concentration in drinkable water may depend on several factors, including the type of organic compounds, free chlorine concentration, pH value, temperature, and contact time and one has to act upon the enumerated factors to minimize their production [10].

In general, both THMs and HAAs are formed when chlorine react with naturally organic materials (NOM) One strategy for controlling formation is to minimize the contact time with chlorine. This control strategy is often by the use of ammonia for converting free chlorine into combined chlorine. Other strategy by reduce NOM in water, Typical NOM removal processes include coagulation; adsorption onto activated carbon, either in the powdered or granular form; adsorption onto specialty resins that are designed for NOM removal; biodegradation within filters or activated carbon adsorbers; and membrane filtration, including reverse osmosis and nanofiltration systems [12].

1.3.4-The Chloramination Process

Ammonia reacts with chlorine to form chloramines which retain disinfection properties. These are known as combined chlorine residuals, and three species are formed depending on the pH and the relative concentration of ammonia to chlorine. These are monochloramine (NH_2Cl), dichloramine (NHCl_2) and trichloramine (NCl_3) are formed in the following reaction [15]:



Mono- and dichloramines resulting from the reaction of chlorine with ammonia in water (equation. 1.4-1.5), it is not commonly used as a primary disinfectant because it is a much weaker and slower acting disinfectant than free chlorine. In some instances, a theoretical contact period of several hours would be required for chloramine to achieve adequate disinfection of certain difficult waters. However, ammonia is sometimes deliberately added after final chlorination to produce a chloramine residual in the water passing into the distribution system. The primary reasons for using chloramines rather than chlorine are: greater persistence of chlorine residual in distribution; reduction in THM and HAA formation; superior control of biofilm growth in the distribution system. The weight ratio of chlorine to ammonia is usually in the range 4:1 to 5:1; when the stoichiometric ratio of 5:1 is exceeded monochloramine is destroyed. Ammonia is added after final chlorination when the free chlorine has acted for the requisite contact time. The reaction is fast, taking only a few seconds to form a combined residual. The most effective pH range for chloramination is 7.5 to 8.5 when. Dichloramine is considered to be a stronger disinfectant than monochloramine but it decays faster. Trichloramine has no disinfection properties and is volatile. An advantage of maintaining residual chloramine in the distribution system is that, if routine examinations show chloramine is present at the ends of the distribution system, this should indicate that no serious pollution has entered the pipes en route. The residual cannot be high enough to disinfect pollution entering the system, but it is useful for monitoring the state of the distribution system. The principal disadvantage of chloramination is the nitrification of any excess ammonia or free ammonia released by the decay of chloramines. This process results in the formation of nitrite in the distribution system by

nitrifying bacteria. Nitrite is toxic. Methods of controlling and preventing nitrite formation include: optimizing the chlorine-to-ammonia ratio, typically 5:1; decreasing residence time in service reservoirs; removing excess ammonia locally by breakpoint chlorination; chlorite addition; reducing natural organic matter; periodic changes to free chlorine; pH control; and re-chloramination of the affected sections to eliminate bacterial growth [17].

Blending of chloraminated water with water containing free residual chlorine in distribution systems can result in breakpoint chlorination or in the formation of dichloramine and nitrogen trichloride, which are well known for causing taste problems. If blending is necessary, it should be carried out upstream of a service reservoir. Barrett (1985) developed a blending model which could be used to predict acceptable blends. Chloramines are not removed by reverse osmosis or deionization which are the processes incorporated in conventional dialysis units. Relevant health professionals should therefore be advised whenever a change is proposed from free chlorine to chloramines. Chloramines can be removed either by granular activated carbon (GAC) installed upstream of the dialysis unit or by chemical reduction with ascorbic acid [17].

1.3.5-Breakpoint Chlorination

The effect of chlorine concentration on the formation of free and combined residuals is best explained by the breakpoint chlorination curve, which is used to ensure that sufficient total chlorine residual is produced Figure 1.2 [15]. Where free chlorine is the sum of hypochlorous acid and hypochlorite ($\text{HOCl} + \text{OCl}^-$), combined chlorine is the sum of all the chloramines ($\text{NH}_2\text{Cl} + \text{NHCl}_2 + \text{NCl}_3$), and total chlorine the sum of both the free and combined residuals.

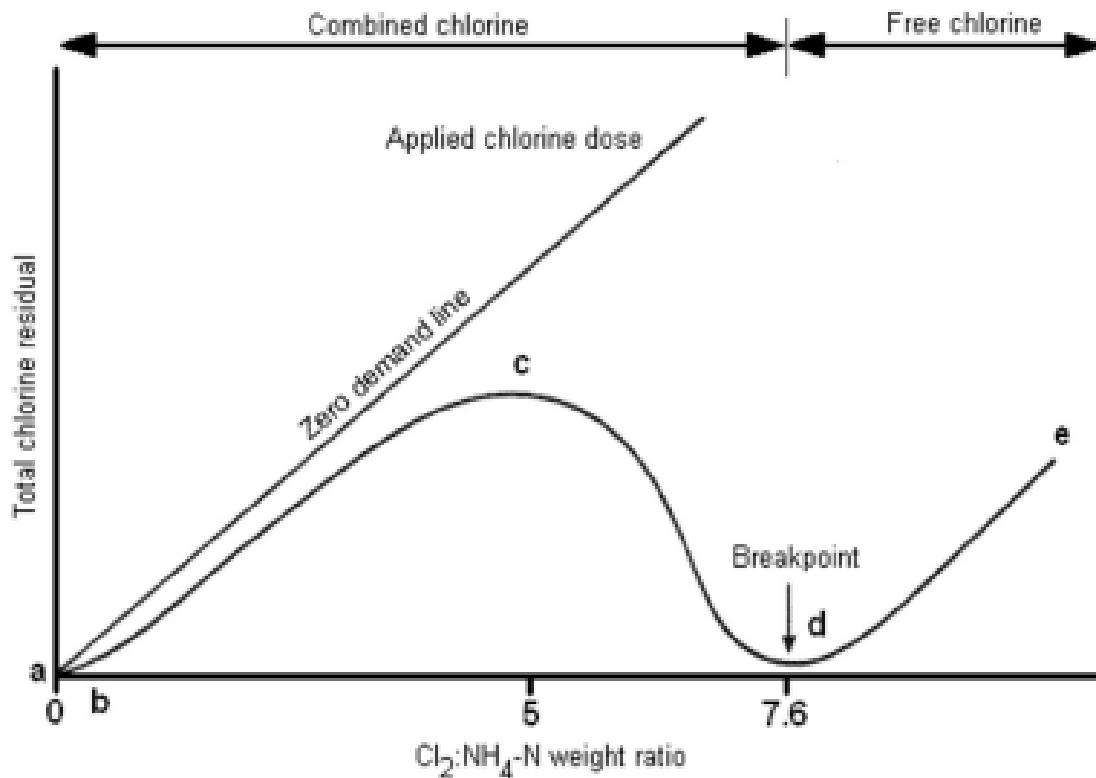
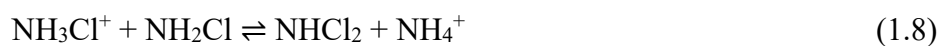


Figure 1.2: Theoretical breakpoint chlorination curve, with the applied chlorine dose equivalent to the zero-demand line when no ammonia or other ions or compound that react with chlorine are present [15].

Iron and Mn exert a chlorine demand Figure 1.2(a-b) so that no residual is produced until this demand is satisfied. The total chlorine residual increases approximately by the amount of chlorine added Figure 1.2(b-c). Where there is no ammonia present this is a straight line with the total chlorine residual comprising of entirely free chlorine being equivalent to the applied chlorine dose. Where ammonia is present then chloramines are formed, producing a combined chlorine residual. This continues up to chlorine to ammonia ($\text{Cl}_2:\text{NH}_4$) ratios of approximately 5.1 (equivalent of a molar ratio of 1) with monochloramine produced where the pH is between 7 and 8. Some dichloramine and traces of trichloramine are produced at the higher $\text{Cl}_2:\text{NH}_4$ dosing ratios and also when the pH is less than 7 [15]:



These reactions are very rapid and are completed with seconds or just a few minutes of contact; although it can take between 10 and 60 minutes for full equilibrium to occur. There are minimal taste or odour problems produced at this weight ratio with no trihalomethane formation. When ammonia is added deliberately (i.e., chloramination) then it is always within this range (i.e., 3–4:1 at pH 7.0–8.5). A disadvantage of chloramination is the nitrification of any ammonia released due to the breakdown of chloramines, resulting in nitrates being formed, which are associated with a number of potential health issues. As the $\text{Cl}_2:\text{NH}_4$ weight ratio increases from 5.1 to 7.6 Figure 1.2(c-d) the total chlorine residual rapidly declines as the excess chlorine oxidizes some of the chloramines present mainly to nitrogen gas but also a portion to nitrate. The point where the lowest total chlorine residual is recorded is known as the breakpoint Figure 1.2(d) beyond which all the residual is of free chlorine which increases in proportion to the amount of chlorine added Figure 1.2(d-e). This occurs at a $\text{Cl}_2:\text{NH}_4$ weight ratio of 7.6 (equivalent of a molar ratio of 1.5) again taking between 10 and 60 minutes for full equilibrium to occur. The precise locations of the $\text{Cl}_2:\text{NH}_4$ weight ratios for the maximum residual and breakpoint to occur is determined by the amount of dissolved organic and reduced substances present. Water supplies that become faecally contaminated, perhaps due to a wastewater treatment plant failure upstream of an abstraction point on a river, may require the chlorine dose to be raised well above that normally used. Normally pre-chlorination is used, but where this is not possible then a very high concentration of chlorine may have to be applied at the end of the treatment process until the problem is resolved. Superchlorination, where very high concentrations are used, must be followed by dechlorination after the required contact period to prevent high concentrations of chlorine entering the distribution system [15].

1.3.6-Dechlorination

Dechlorination can be described as the practice of removing all or a specified fraction of the total chlorine residual. In potable water, dechlorination is used to reduce the residual to a specified level at the point where the water enters the distribution system. [Howard and Thompson] were among the first to report the earliest dechlorination effort for potable water treatment. Their study focused on the removal of taste and odor from chlorine residuals in Toronto's water supply. Chlorination followed by dechlorination is widely used in Britain. Its principal use is for the disinfection of underground supplies where contact time is short. By using the chlorine residual contact time concept [12].

dechlorination is achieved by injecting either sulphur dioxide (SO_2) or sodium bisulphite (NaHSO_3). Sufficient residual chlorine must be left after dechlorination as the water enters the distribution network, so careful additions of these chemicals are required. Sulphur dioxide is a gas with 0.9 mg theoretically removing 1.0 mg of chlorine, while the liquid sodium bisulphide is applied at a stoichiometric ratio of 4.5 mg (20% wt. SO_2) per 1.0 mg of Cl_2 removed. In practice up to 15% more of either of these chemicals may be required. Granular activated carbon filtration or hydrogen peroxide can both be used as alternative dechlorination methods. The dosing rate of chlorine required depends on a large number of factors such as the ammonia concentration, pH, concentration of dissolved organic matter, the concentration of iron and manganese, the rate of flow and the chlorine residual required after contact, which is generally between 0.2 and 0.5 (mg/L) after 30 minutes to ensure an optimum pathogen inactivation rate. Chlorination results in a strong taste and odour in treated water and is the commonest source of complaint from consumers. The average taste threshold value is pH dependent being 0.16 (mg/L) at pH 7 but increasing to 0.45 (mg/L) at pH 9. All these factors, including the prevention of DBP formation, must be taken into account when calculating the residual chlorine required and the actual chlorine dose [15].

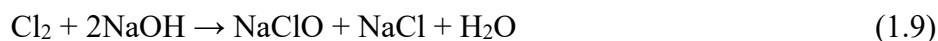
1.4-Sodium Hypochlorite Production Types

Some years after the discovery in (1774) of the gas called 'dephlogisticated salt spirit' by the Swedish chemist Carl Wilhelm Scheele, another chemist, the Frenchman Claude-Louis Bertholet obtained in (1787) some bleaching solutions of this gas dissolved in water. In (1810) this gas was renamed 'Chlorine' by the Englishman Davy. A small chemical industry in Paris directed by Leonard Alban, the 'Société Javel', adopted the Bertholet process for the industrial production of a bleaching solution produced by dissolving gaseous chlorine (Cl_2) in water. The factory was built in (1778) on the banks of the Seine. In (1787) the process was modified, and the chlorine, rather than being dissolved in water (to form an unstable though very active solution of hypochlorous acid, was made to react in a suspension of 'washing soda'. After filtration, a solution is obtained that is still effective in bleaching and much more stable, to which Alban gave the name of 'Eau de Javel'. In (1820) Labarraque used caustic soda (NaOH) which is more economical, and obtained the solution of NaClO that was called 'Eau de Labarraque', which found wide use as a disinfectant and bleaching agent [18].

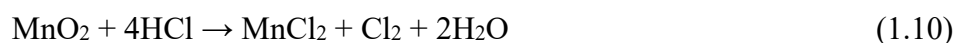
Generally, there are two methods to produce sodium Hypochlorite (NaClO), the chemical and the electrochemical method.

1.4.1-The Chemical Method

In industrial plants, Cl₂ is made to react with a solution of NaOH so the sodium hydroxide absorbs the chlorine gaseous like shown in (Eq. 1.9) [18].



the chlorine used here was produced by heated manganese dioxide with hydrochloric acid (Eq. 1.10) [12]:



This method produces solutions of high concentrations, but their purity and stability do not satisfy the quality characteristics that are necessary for their use in the food and medical sectors. [18].

1.4.2-The Electrochemical Method

The basis of the electrochemistry was founded with the discovery of electricity sources by L. Galvani and A. Volta at the end of the 18th century. With the earlier known electrostatic machines it was not possible to run an electrolysis experiment over a long period. In (1834) Faraday postulated the fundamental laws of electrochemistry [19]:

- the weight of a given element formed at an electrode is directly proportional to the charge passed through the solution (the unit of charge is the coulomb).
- the weights of different elements formed by the same quantity of electricity are proportional to the equivalent weights of the elements.

The electrochemical method can be divided into two processes, the chlor-alkali process, and the on-site generation process.

1.4.2.1-The Chlor-Alkali Process

It was the first to prepare chlorine electrochemically; however, the process was of little significance until the development of a suitable generator by SIEMENS and of synthetic graphite for anodes by ACHESON and CASTNER in (1892). These two developments made possible the electrolytic production of chlorine, the chlor-alkali process, on an industrial scale. About the same time, both the diaphragm cell process (1885) and the

mercury cell process (1892) were introduced. The membrane cell process was developed much more recently (1970). Currently, more than 95% of world chlorine production is obtained by the chlor-alkali process. Since (1970) graphite anodes have been superseded by activated titanium anodes in the diaphragm and mercury cell processes. The newer membrane cell process uses only activated titanium anodes [20].

In the chlor-alkali electrolysis process, an aqueous solution of sodium chloride is decomposed electrolytically by direct current, producing chlorine, hydrogen, and sodium hydroxide solution.

The overall reaction of the process:



takes place in two parts, at the anode and at the cathode. The evolution of chlorine takes place at the anode:



There are three basic processes for the electrolytic production of chlorine, the nature of the cathode reaction depending on the specific process. These three processes are: the diaphragm cell process, the mercury cell process, and the membrane cell process. Each process represents a different method of keeping the chlorine produced at the anode separate from the caustic soda and hydrogen produced, directly or indirectly, at the cathode [20].

A-Mercury Process

In the mercury cell process, sodium amalgam is produced at the cathode. The amalgam is reacted with water in a separate reactor, called the decomposer, to produce hydrogen gas and caustic soda solution.

Because the brine is recirculated, solid salt is required for resaturation. The brine, which must be quite pure, is first dechlorinated and then purified by a straightforward precipitation-filtration process [20]. more details shown in Figure 1.3 [21].

The products are extremely pure. The chlorine, along with a little oxygen, generally can be used without further purification. The sodium hydroxide solution contains little chloride and leaves the decomposer with a 50 wt % concentration. Of the three processes,

the mercury process uses the most electric energy: however, no steam is required to concentrate the caustic solution. The use of large quantities of mercury demands measures to prevent environmental contamination. In addition, the hydrogen gas and sodium solution must be freed from mercury. Generally, the operation of the cells is not simple [20].

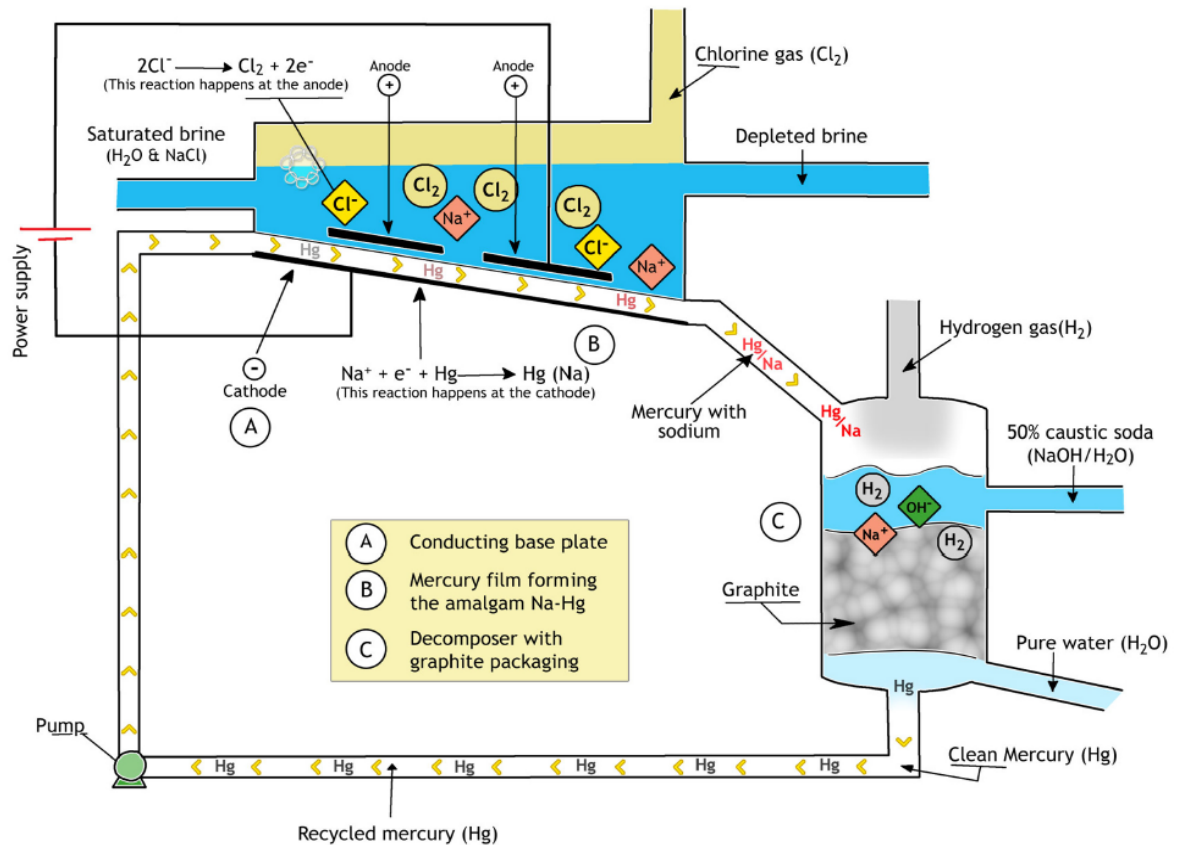


Figure 1.3: Mercury cell process [21].

B-Diaphragm Process

In the diaphragm cell process, the anode area is separated from the cathode area by a permeable, generally asbestos-based diaphragm. The brine is introduced into the anode compartment and flows through the diaphragm into the cathode compartment. Cheaper solution-mined brine can be used; the brine is purified by precipitation - filtration. A caustic brine leaves the cell, and this brine must be freed from salt in an elaborate evaporative process. Even so, the resultant 50 wt % sodium hydroxide solution contains up to 1 wt% NaCl. The salt separated from the caustic brine can be used to saturate dilute brine. The

chlorine contains oxygen and must be purified by liquefaction and evaporation [20]. more details shown in Figure 1.4 [22].

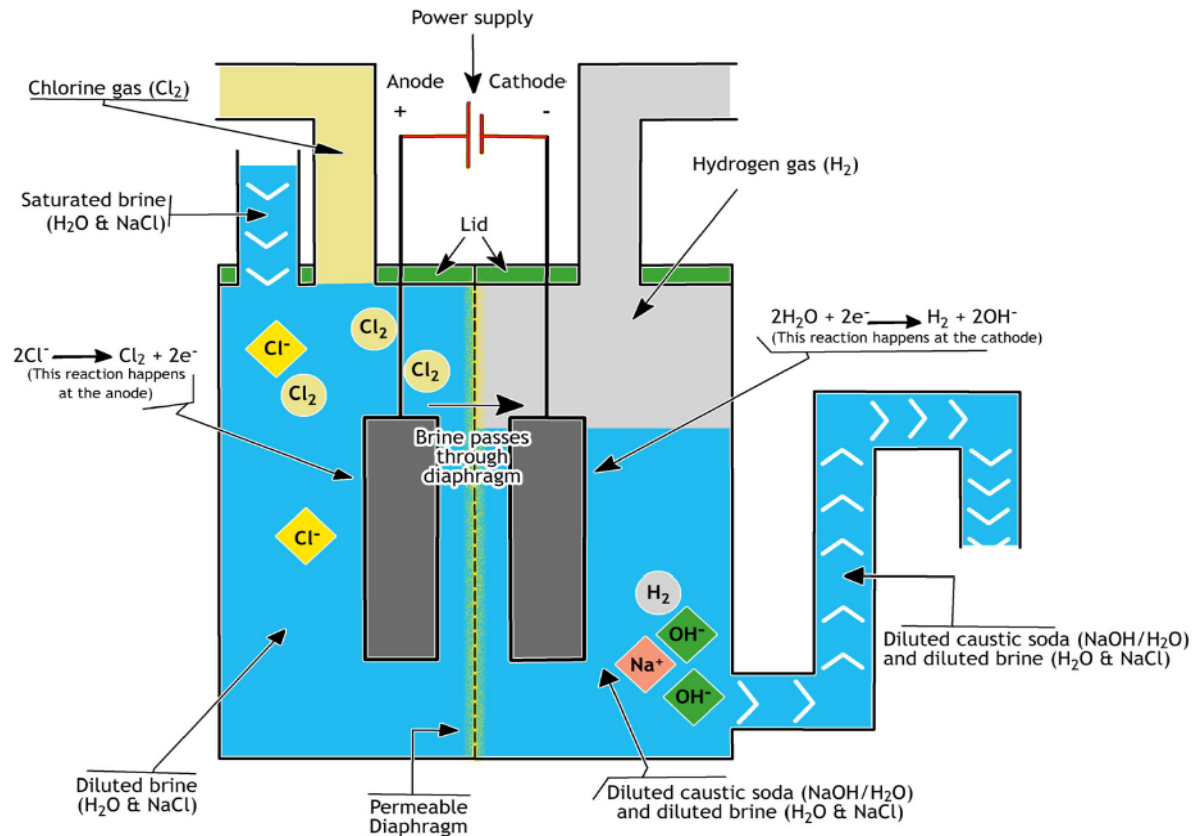


Figure 1.4: Diaphragm cell process [22].

The consumption of electric energy with the diaphragm cell process is 15 % lower than for the mercury process, but the total energy consumption is higher because of the steam required to concentrate the caustic brine. Environmental contamination with asbestos must be avoided. Under constant operating conditions, cell operation is relatively simple [20].

C-Membrane Process

In the membrane cell process, the anode and cathode are separated by a cation permeable ion-exchange membrane. Only sodium ions and a little water pass through the membrane. As in the mercury process, the brine is dechlorinated and recirculated, which requires solid salt to resaturate the brine. The life of the expensive membrane depends on the purity of the brine. Therefore, after purification by precipitation - filtration, the brine is

also purified with an ion-exchanger. The caustic solution leaves the cell with a concentration of 30 - 36 wt % and must be concentrated. The chloride content of the sodium hydroxide solution is almost as low as that from the mercury process. The chlorine gas contains some oxygen and must be purified by liquefaction and evaporation [20]. more details shown in Figure 1.5 [23].

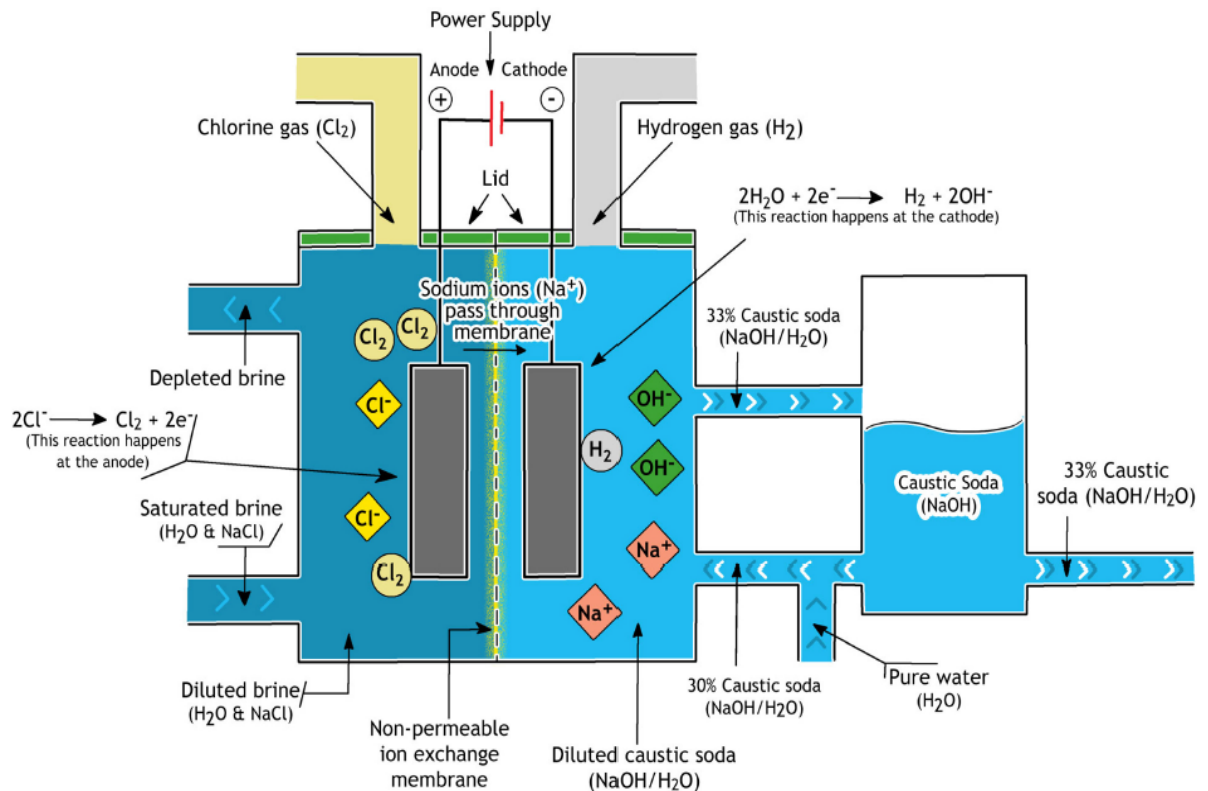


Figure 1.5: membrane cell process [23].

The consumption of electric energy with the membrane cell process is the lowest of the three processes, 25 % less than for the mercury process, and the amount of steam needed for concentration of the caustic is relatively small. The energy consumption should be even lower when oxygen-consuming electrodes become common [20].

Beside the low consumption of energy between the three processes, the membrane cell is the most modern technology, and the safest comparing to the other two who use mercury and asbestos.

1.4.2.2-On Site Generation

On-site generation (OSG) of hypochlorite in the United States was largely inspired by the use of hypochlorite solution during World War I (1914–1918). This solution became known as the Carrell-Dakin solution. Its success in the antiseptic treatment of open wounds led to the on-site generation of this solution in hospitals. While on-site generation was feasible at the turn of the twentieth century, the limitation was the electrode materials, carbon or platinum, the former which would dissolve in service, causing cell damage and poor product quality, and the latter too expensive for practical use. No cell developed during this period, not until (1950). Two major technological breakthroughs in the (1950s) fostered a quantum change in the types of electrodes for the chlorine industry and subsequently on-site hypochlorite generation systems. First, in the (1950s), titanium became commercially available in large quantities. The excellent corrosion resistance of titanium in a variety of solutions and its self-oxidizing metal characteristics became key in electrochemical systems. The second major breakthrough was the development of the dimensionally stable anode (DSA) by Henri Beer. In (1965), Henri Beer coated titanium with catalytic materials, such as ruthenium and iridium, and then heated the components. The process created a dimensionally stable, long-lasting anode that ultimately spurred the chlor-alkali and on-site hypochlorite generation industry. The relatively low cost of these DSAs fueled innovation to develop comparably low-cost, efficient electrolytic cells and systems in the early (1970s) [13].

Recent advances in OSG technology and increased concerns regarding the security and safety risks associated with chlorine gas have resulted in on-site generation of sodium hypochlorite becoming a more attractive and cost-effective option. Advantages of on-site generation over chlorine gas and bulk hypochlorite can include [13]:

- Reduced volume of hazardous material that must be stored on-site
- Improved safety for the public and plant personnel
- Elimination of liabilities associated with transportation of hazardous materials

The OSG system can be divided into two systems, the separated and the unseparated system.

A-The Separated System

Or the high-strength OSG systems use an anode and cathode that are separated by an ion exchange membrane that permits electrical conductivity in the brine but eliminates mixing of the solution on the anode side (anolyte) with the solution on the cathode side (catholyte). As electrolysis proceeds, the pH in the anolyte drops, allowing Cl_2 gas to evolve unassisted or to be removed by air-sparging. On the cathodic compartment of the cell, the caustic product can be produced to concentrations as high as 15% by weight. Cl_2 gas produced by this type of OSG system may either be collected at atmospheric pressure and directly injected into the water to be treated or combined with the caustic product from the cathodic process to yield a high-concentration (up to 15% by weight) hypochlorite solution, which is then used in the same fashion as bulk delivered hypochlorite. In the latter case, the sodium hydroxide feed must often be supplemented with additional sodium hydroxide to achieve the desired pH of the hypochlorite solution. OSG systems of this type often have higher maintenance requirements due to fouling of the membrane dividing the anode and cathode compartments [13].

B-The Unseparated System

Which known as the low-Strength OSG Systems. This, systems produce AC concentrations of ~ 8 (g/L) (0.8% w/w) and use NaCl brine concentrations of 15–30 g/L (9–18 g/L Cl^-). The solution flow rates and daily volumes produced at these AC concentrations are sufficient for use in potable and industrial water treatment operations and swimming pools. Many OSG systems are modular so that large masses of AC can be produced daily from the total system of several modules [13].

The low strength OSG is the most usable system in the water treatment and disinfection field, which is our main topic in this work, this system will be covered in more detail in chapter 2.

C-Other Types of OSG Systems

Several other types of OSG systems also exist but are not deployed for municipal water treatment applications. These OSG systems include seawater OSG systems that produce chlorine directly from the sodium chloride naturally occurring in seawater, divided-cell OSG systems that use physical barriers to divide the anolyte and catholyte streams inside

of a monopolar electrolytic cell, and batch OSG systems that produce chlorine in a batch mode as opposed to a flow-through geometry [13].

CHAPTER 2
ON SITE GENERATION

Chapter 2: On Site Generation

2.1-Process Overview

The low strength On-site generation is a technology that use electricity to oxidize chloride ions from the sodium chloride in the brine solution, and then start a series of reaction end with sodium hypochlorite.

The process started with softened water generated from the softener, the water will split into two streams with one goes to salt dissolver to prepare saturated brine solution from sodium chloride and water, with a concentration in the range of 300 to 358 (g/l), then it will be pumped to the electrolytic cell with brine pump, while the other stream will be used in the dilution of the brine solution to a concentration of 30 (g/l), the dilution may occur before or after entering the electrolytic cell it depends on the technology. Inside the electrolytic cell, the sodium hypochlorite production start with a direct current pass through the brine solution to form the final product with the overall reaction [13]:



And the basic reactions of the process are the following:

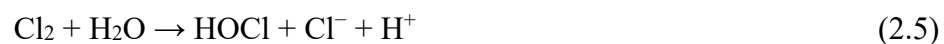
at the anode:



At the cathode:



The chlorine that produced at the anode will dissolve immediately in water to form a hypochlorous acid and other ions:



Then the hypochlorous acid will react to form hypochlorite ions:



In the undivided cell of most OSG systems, in which the solutions at the anode and cathode are free to mix, the hydroxide ions that are produced at the cathode will combine with the acids produced at the anode, resulting in the formation of hypochlorite



By rewriting these equations for both charge and molar balance, the overall chemical transformation described in (equation 2-1) is realized. As shown in the Figure 2.1 [13].

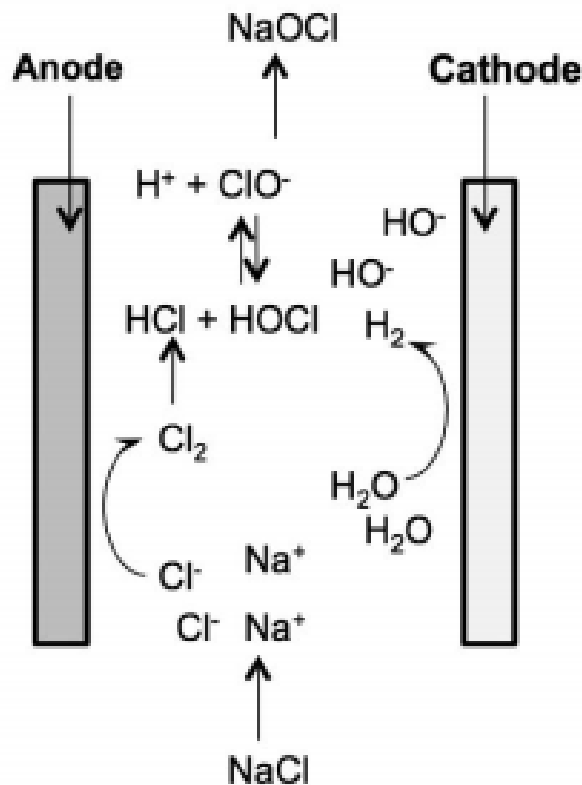


Figure 2.1: The basic reaction that occurred on electrodes surfaces in the unseparated cell [13].

The chlorine species contain in the solution vary depend on pH of the electrolyte as shown in the Figure 1.1 [13]. Acidic to slightly basic conditions tend to favor the generation of hypochlorous acid, whereas higher pH tend to shift the equilibrium toward hypochlorite species. At pH values above 10, the equilibrium is shifted such that hypochlorite is the predominant species in the solution [24].

Beside those reactions there is other reaction known as parasite reaction which affect the current efficiency, the cell lifetime and production of sodium hypochlorite. more detail in the following Sections.

The produced sodium hypochlorite solution will then flow to a temporary storage tank to handle the hydrogen gas by a blower before launched it the environment.

Finally, the solution produced which has a free available chlorine concentration of 0.8% or 8 (g/l), is ready to use for disinfection.

2.2-Equipments

In this section we will talk about the equipment that used in the OSG process [13]:

- Water softener: Essential for removal of calcium and magnesium from the feed water;
- Salt dissolver/brine tank: Provides the required salt solution for electrolysis;
- Brine feed equipment: Brine pumps to control brine flow into the electrolyzer cell;
- Electrolysis cell or cells: Electrolyzes the dilute brine solution;
- DC power rectifier: Provides the direct current for electrolysis;
- Storage tanks: Product storage to meet dosing requirements as well as any excess capacity essential to ensure continuous dosing capabilities. Note: In rare cases, facilities may directly dose, negating the need for a storage tank;
- Hydrogen mitigation system: Provided to vent the by-product hydrogen gas produced during the electrolysis process to the outside of a building;
- Dosing pumps with dosing controls: Provides the needed disinfection dose based upon the chlorine residual and/or flow rate of a receiving stream;
- Cell cleaning system: Used to remove the calcareous material deposited on the cell cathodes during the production process;
- heater/chiller water system: used to control temperature of the solution;

The Figure 2.2 [13], shown a design for OSG system.

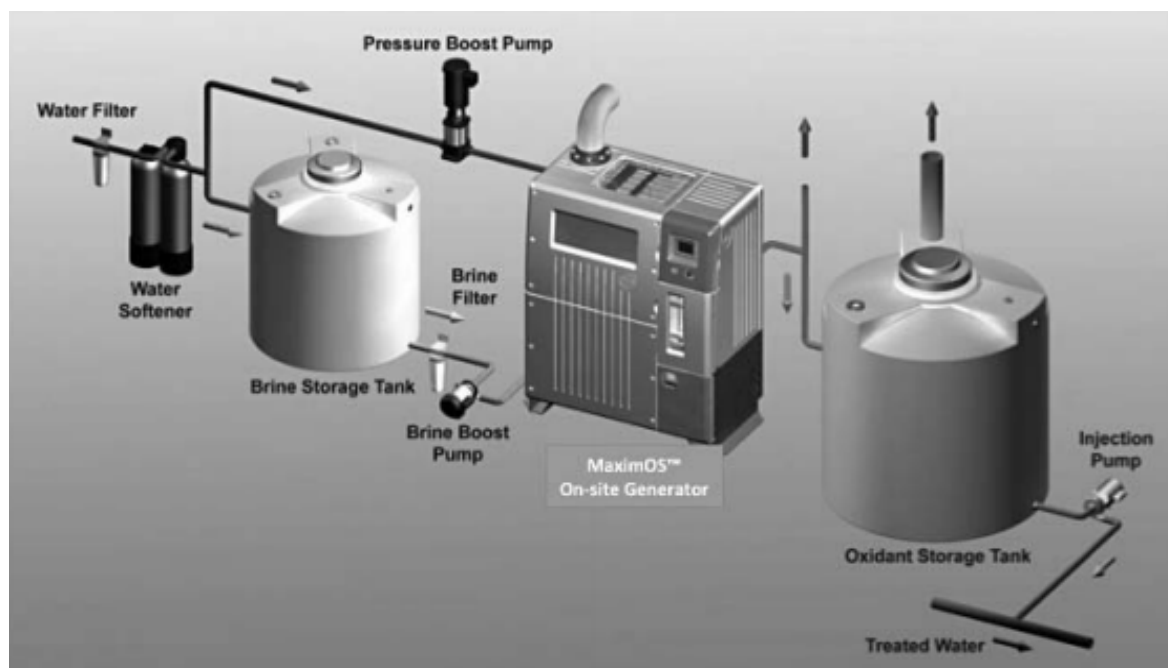


Figure 2.2: MaximOS process flow diagram [13].

2.3-Optimization of The Process

The process should operate at the optimum to obtain a high conversion of brine to sodium hypochlorite, and high current efficiency, for better use of equipment, materials, and electricity.

Current efficiency is defined as the amount of product actually produced divided by the amount of product that theoretically should have been produced on the basis of the amount of direct-current electrical energy input. The current efficiency is never 100% because of side reactions [20], so we should try to enhance the brine conversion, reduce parasite reaction, and choose the optimal operating condition.

We can approach these goals by optimizing the following parameters:

2.3.1-Brine Solution

The brine solution made of sodium chloride NaCl and water. The salt used was the same table salt, but in the brine preparation for OSG system we can't use the table salt due

to the presence of impurities like ions of Fe, Cu, Ba, Co, Ni, Mg, Ca, etc., that will adversely affect the process, for example at low concentration ions of Fe, Cu, Ni and Co may catalyze the decomposition reactions of hypochlorite. A concentration of 1 (mg/l). of Fe respectively 1 (mg/l) of Ni in the solution is enough to affect the acceleration of the decomposition reaction of hypochlorite [25].

Experimental results have shown that the presence of Ca^{2+} and Mg^{2+} in the salt solution may disturb the electrolytical process by forming deposits of $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ at the electrodes when the pH in the cell is 11. These deposits would cause clogging of the solution exit of the cell, giving a decrease in the current efficiency as the overall result [25], it will also reduce the cleaning efficiency due to these insoluble deposit at the electrodes.

This is why salt refining is needed, or by buying a pure salt directly to avoid impurities problems. The typical value of salt for the process is described in Table 2.1 [26].

Table 2.1: The typical value of salt required for electrical cell [26].

Components	Typical values
NaCl	99.72%
Fe^{2+}	< 1 (mg/l)
Cu^{2+}	< 0.5 (mg/l)
Ca^{2+}	400 (mg/l)
Mg^{2+}	120 (mg/l)
Total sulphate	1200 (mg/l)
Insoluble matter	200 (mg/l)

Water also should be treated using water softener due to its hardness, calcium and magnesium ions in the water can develop into a hard scale in piping systems and other equipment. In OSG systems, the scale will coat the electrodes in the cells and, over time, reduce their efficiency, thus increasing their electricity demand. It can also inhibit flow

through the cell and cause blockage. When the sodium hypochlorite and hydrogen cannot exit the cell, pressure will rise and, if ignored, the cell may burst. Ideally, water hardness for OSG systems should not exceed 17 (mg/l) as CaCO_3 [12].

NaCl concentration also affect the AC production. Figure 2.3 [18], indicates how the cell production of active chlorine depends on electrolyte concentration. For every type of anode studied, there is an increase of AC with increase in electrolyte concentration. The cell potential diminishes with increasing concentration of electrolytes in solution, and this increase is more marked for graphite than for the other materials. As observed for the effect of temperature, the Ti/Pt and Ti/RuO₂ anodes give results appreciably better than those of graphite. However, it is known that, for industrial production of NaClO it is always appropriate to work with brine of high concentration [18], and with concentration of 30 (g/l) for low-strength OSG.

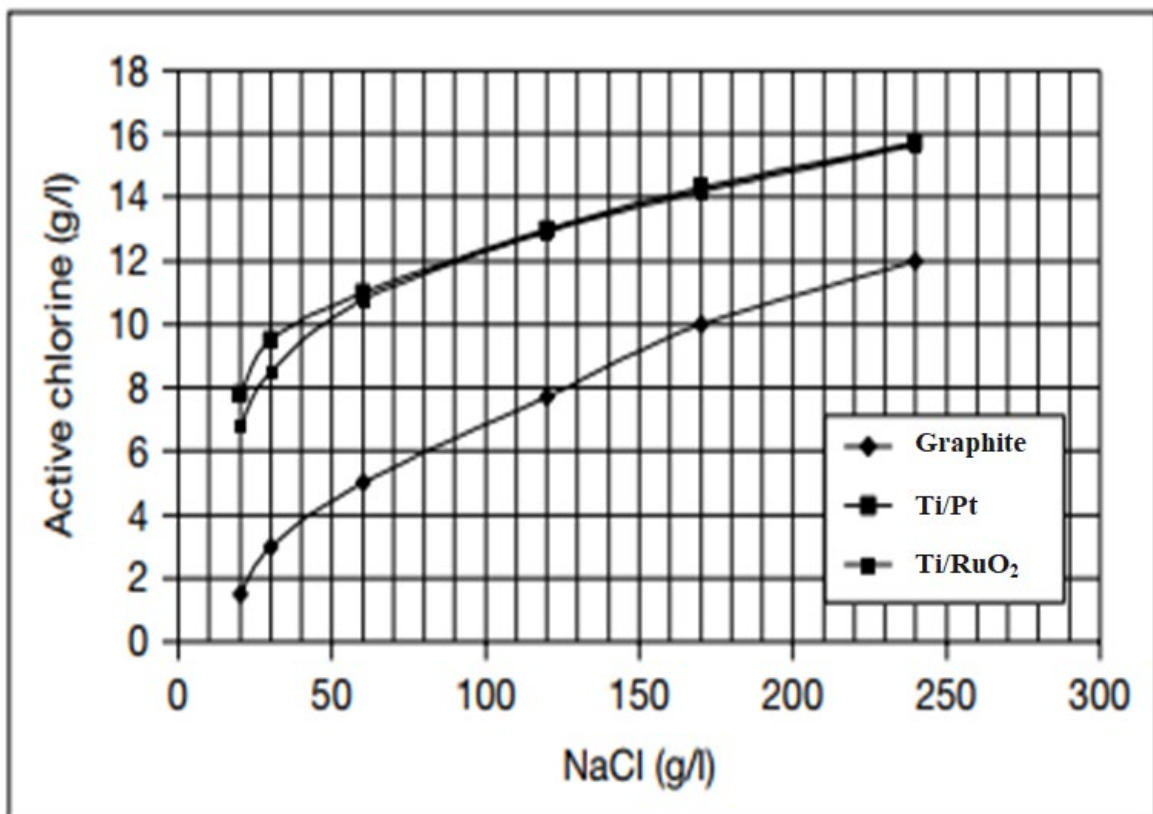


Figure 2.3: Effect of NaCl concentration as a function of the type of the anode [18].

Ti cathode; current density 10 A/dm^2 ; temperature 20°C; electrolysis time 1h.

2.3.2-pH

The pH plays a big role in both process and storage of sodium hypochlorite, in the process part the best pH for dissolving salt, is in the range of 7-9. In many systems, the stability of pH control is more important than the exact value. If there is continual fluctuation in pH, certain impurities will dissolve more freely at a particular pH and then precipitate in downstream equipment. It is said, soluble magnesium species become insoluble when mixed with the alkaline brine [27], which increase the insoluble matter and so the efficacy of cleaning.

As shown on Figure 1.1 the pH of the solution has negative as well as positive influences on the process. At low pH most of the hypochlorite exists in its acid form, so that the possibility of the occurrence of the reaction consuming (OCl^-) at that pH is diminished, conversely the reaction for the formation of chlorate (ClO_3^-) is accelerated. Each variable, whatever value it has seems to exert some influences which have contradictory effects. It is therefore highly recommendable that for any hypochlorite cell the optimum operation variables be determined experimentally [25].

2.3.3-Temperature

The effect of temperature is crucial for the whole process and a temperature sensor is required to detect any drop or rise in temperature degrees. The Brine systems are susceptible to water temperatures less than 15°C [11], which is why a water heater is needed in the case of temperature drop below 15°C .

whereas operating at high temperature increases the formation of chlorate (ClO_3^-) and the consumption of the electrodes resulting in the accelerated deterioration of electrodes. [25], it is always indispensable to work at temperatures less than 40°C to prevent the formation of chlorate [18], and so a water chiller is needed to keep the temperature below 40°C .

In a sodium hypochlorite solution, additional energy as heat, will increase the rate of reaction. In general, chemists predict that a 10°C rise in temperature will double the rate of most chemical reactions. However, studies with sodium hypochlorite have shown that for every 10°C rise in temperature, the decomposition rate increases by a factor of 3–4 in a solution of 5–16 weight percent hypochlorite. Sodium hypochlorite stored at 15°C will degrade at a rate 14 times more slowly than at 35°C . Additionally, at a temperature of 5°C ,

in the absence of heavy metal contamination, degradation is almost completely eliminated. Accordingly, there is tremendous advantage to managing the storage temperature of sodium hypochlorite solutions. The temperature effect and the concentration effect are further illustrated in Table 2.2. Some sodium hypochlorite manufacturers will rapid-cool their product after manufacture to stabilize the degradation by lowering its temperature [12].

Table 2.2: Storage temperature of sodium hypochlorite solutions [12].

Trade %	Half-life (days)	
	25°C	35°C
15	144	39
12	180	48
9	240	65
6	360	97
3	720	194
1	2160	580

the effect of temperature is not always negative, but it has its positive effect for example; an increase of the solution temperature may result in an increase of the electric current as well [25], and in the brine conversion. Based on the Faraday efficient plot Figure 2.4 18.75°C is the optimal degree or the closest value [12].

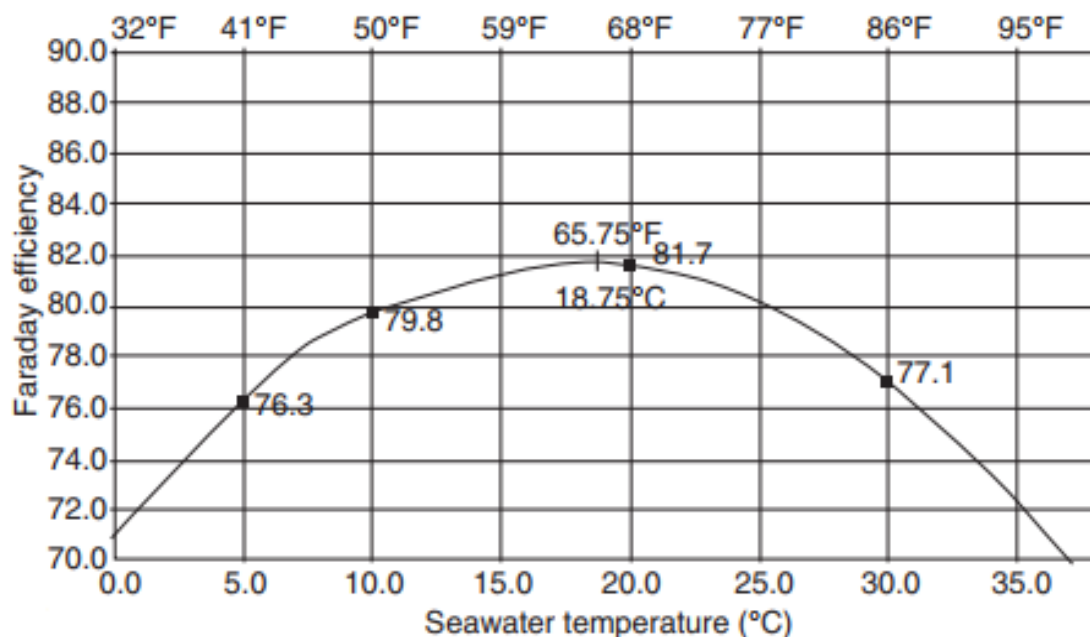


Figure 2.4: impact of temperature on the efficiency of the electrolysis process [12].

Also, another experiment of M. A. Aziz et al. they found from Figure 2.5 temperature of 22°C favors the formation of sodium hypochlorite [28].

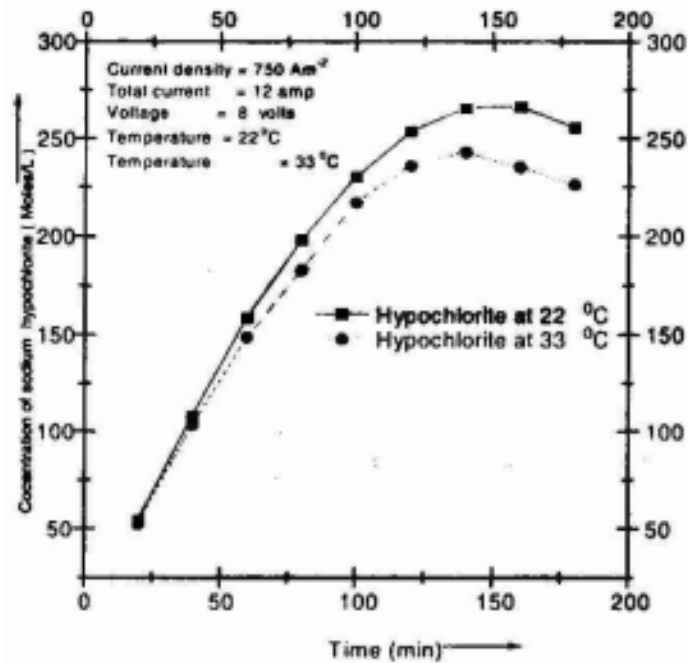


Figure 2.5: Variation of concentration of sodium hypochlorite with time at different temperatures[28].

The ideal temperature depends on the electrolytic cell technology and other parameters which mean experiments must be done to find out what is the optimal temperature.

2.3.4-Flow Rate

For a given hypochlorite cell there exists an optimum electrolyte flow rate giving the highest current efficiency. At low flow rate the diffusion of Cl^- ion to the anode is slow and thus the rate of the hypochlorite formation is also slow. Conversely at very high flow rate the possibility for Cl_2 to reach the surface of the cathode and for OCl^- to reach the surfaces of the anode and the cathode is increased. In such a case the reversed reaction of Cl_2 producing Cl^- ion at the cathode, and degradation of OCl^- and production of chlorate (reaction 2.10) at the anode, as well as degradation of OCl^- to Cl^- and OH^- (reaction 2.11) at the cathode cannot be avoided. However at high solution flow rate the deposition of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ at the cathode surface is reduced, and this induces some advantages. First the current efficiency can be increased and second the frequency for washing the cell with acid is reduced resulting in a longer life of the electrodes [25].

2.3.5-Best Choice of Electrodes

The electrodes are the most important pieces in the electrolytic cell, which make the energy in the form of electricity converted to a chemical energy (in a form of reaction) that lead us to the desired product. Due to the importance of the electrodes and their impact to the process there is a need for studies and experiments to choose the best type of electrodes and the right operating system, below are the most important parameters:

2.3.5.1-Types of Electrodes

At the end of the sixties two discoveries made a cheaper production of caustic soda and chlorine possible. One of them is ‘dimensionally stable anode’ (DSA), developed by Henri Beer in (1968s), is a very stable electrode in the corrosive chloride/chlorine solution. Furthermore, this electrode has a much lower overpotential than the earlier carbon anodes with respect to the chlorine evolution [19].

Previously, graphite anodes had been applied, but these electrodes were consumed during use, requiring frequent adjustment of the anode position. Beer realized that since titanium forms a highly corrosion-resistant TiO_2 oxide layer when used as an anode, it could be used as a stable anode support material in chlor-alkali electrolysis [29].

In fact, graphite electrodes release micro- and nano-particles of graphitic carbon that are very difficult to eliminate even with sophisticated filtration methods. These impurities represent one of the main causes of instability of NaClO , which decomposes starting from the surface of these particles, which function as catalysts for the decomposition reactions. With DSA-type anodes (e.g., Ti/RuO_2), the solution proves particularly pure and free of particles in suspension and is stable for very long periods. The common electrodes used in electrochemical cells for the production of NaClO are [18]:

- Anode: graphite (not advised), titanium with a platinum coating (Ti/Pt) (good), titanium with a coating of ruthenium oxide (Ti/RuO_2) (excellent);
- Cathode: graphite (not advised), stainless steel or nickel (risky), Ti (good), titanium coated with iridium oxide (very good).

2.3.5.2-Electrodes Sizes

Figure 2.6 shows the effects of the ratio of the surface areas of the electrodes on the production of active chlorine. First of all, it is noted that, with increasing S_a , AC increases in an almost linear manner, up to an optimal value. The maximum value of AC is found at an optimal value of the S_a/S_c ratio of 1.33, after which AC decreases. This is in agreement with what is described in the literature, which indicates how $S_a > S_c$ favors the production of AC. In fact, a large S_a promotes the transformation of chloride ions into hypochlorite ions, while a small S_c works against cathodic reduction of the same hypochlorite ion [18].

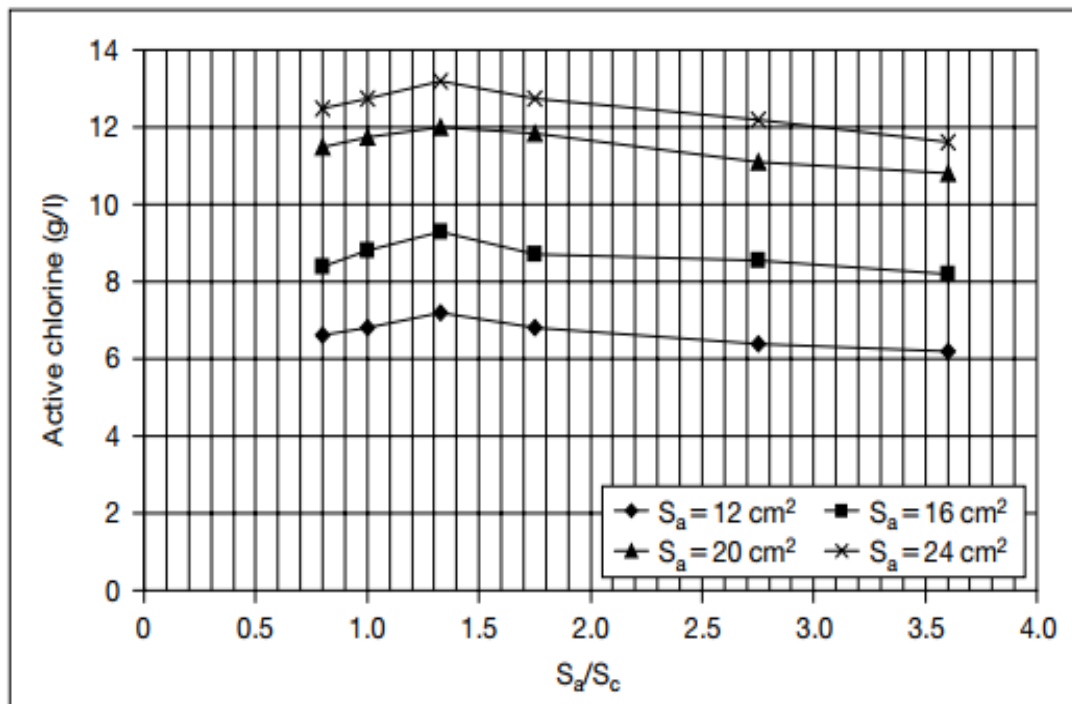


Figure 2.6: Effect of S_a/S_c ratio [18].

Ti/TiRuO₂ anode; Ti cathode; current density 10 A/dm²; NaCl concentration 2M;
temperature 20°C electrolysis time 1h

With:

S_a : anode surface ;

S_c : cathode surface ;

AC : active chlorine in solution.

2.3.5.3-Inter-electrodes Distance

By decreasing the distance between the electrodes, the current efficiency is increased, and the time for the ClO^- ion to travel to the electrode's surface is shortened as well resulting in the acceleration of reaction (Reaction. 2.10) at the anode and reaction (Reaction. 2.11) at the cathode [25].

Figure 2.7 illustrates the variation of AC as a function of the inter-electrode space, for an optimal value of $S_a/S_c = 1.33$. As seen in the figure, AC decreases as the distance between anode and cathode increases. The maximum AC concentration is obtained with an anode-cathode distance of 8 (mm); and after 20 (mm), AC decreases abruptly. This observation is in line with the idea that a small distance should favor the conversion of Cl^- to ClO^- inasmuch as it minimizes the ohmic potential drop and therefore increases the current density of the cell. At this point, it can be said that the optimal conversion of Cl^- into ClO^- takes place with a S_a/S_c ratio = 1.33 and for an inter-electrode distance less than 0.8 cm. The following graphs have been obtained from tests done with the optimal cell parameters of $S_a/S_c = 1.33$, $S_a = 24(\text{cm}^2)$ and a distance between the electrodes of 0.5 (cm) [18].

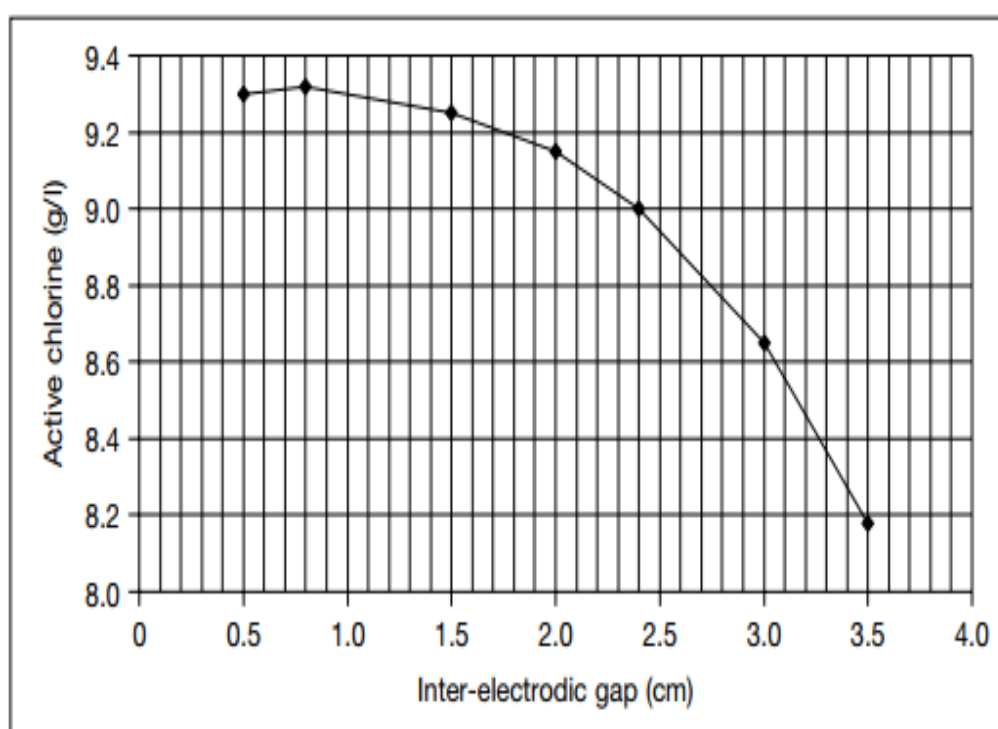


Figure 2.7: Effect of inter-electrode gap [18].

Ti/TiRuO₂ anode; Ti cathode; $S_a/S_c=1.33$; current density 10 A/dm²; NaCl concentration 2M; temperature 20°C; electrolysis time 1h.

2.3.5.4-Effect of type of Anode

The electrodes most used as anodes in electrolysis cells for production of hypochlorite are (Ti/Pt) and (Ti/RuO₂), in as much as their perfect resistance to corrosion permits working at high current densities. Figures (2.3 and 2.8) report the behavior of these anodes during electrolysis in comparison with traditional graphite anodes [18].

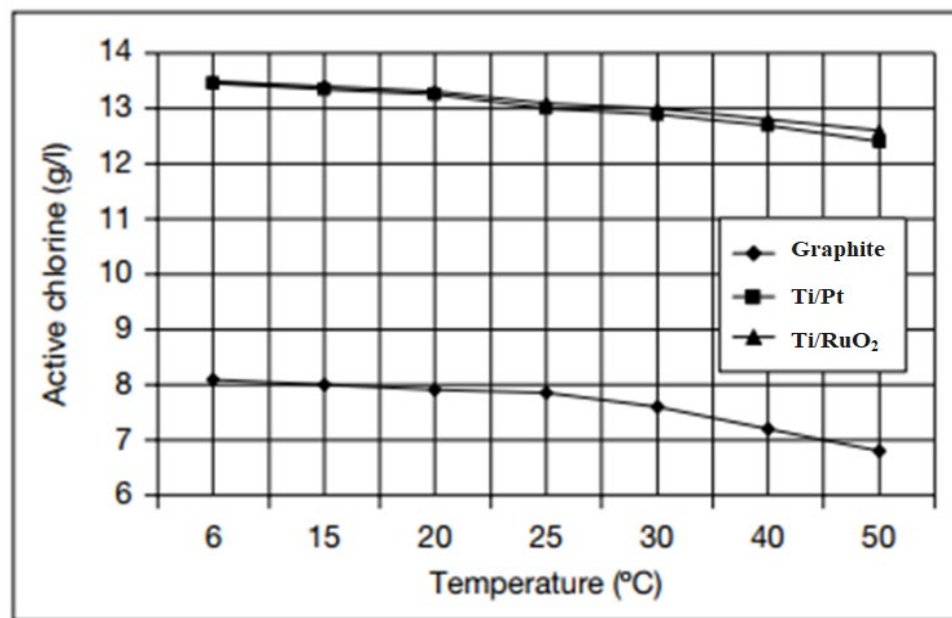


Figure 2.8: Effect of temperature as a function of the type of the anode [18].

Ti cathode; Sa/Sc = 1.33cm; current density 10 A/dm²; NaCl concentration 2M; electrolysis time 1h.

2.3.5.5-Effect of Type of Cathode

The behavior of four different types of cathodes has been analyzed: graphite, stainless steel, nickel and titanium. Figures (2.9 and 2.10) [18], illustrate how AC depends on the electrolysis time and on the current density applied, respectively, using DSA electrodes of Ti/RuO₂ as anode.

The experimental curves of each figure are almost superimposable. This indicates little influence of the cathode composition on AC. However, the future of the cathode influences the behavior of the cell, acting both on the reduction reaction of the hypochlorite ions and on the cathodic overload of hydrogen development. We can deduce from figure 2.9 that the active chlorine is produced at a speed of about 0.2 (g/l) per minute for the first 130 (min) of electrolysis. After that, the speed diminishes to zero, and production settles at AC = 30 (g/l).

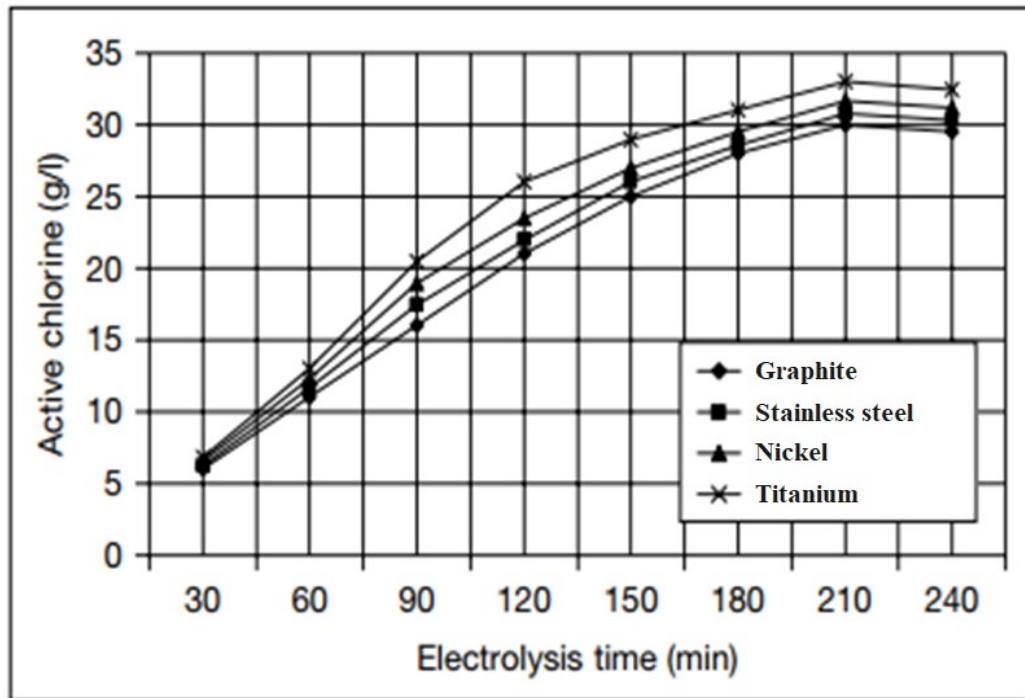


Figure 2.9: Effect of electrolysis time as a function of the type of the cathode [18].

Ti/TiRuO₂ anode; current density 10 A/dm²; NaCl concentration 2M; Temperature 20°C.

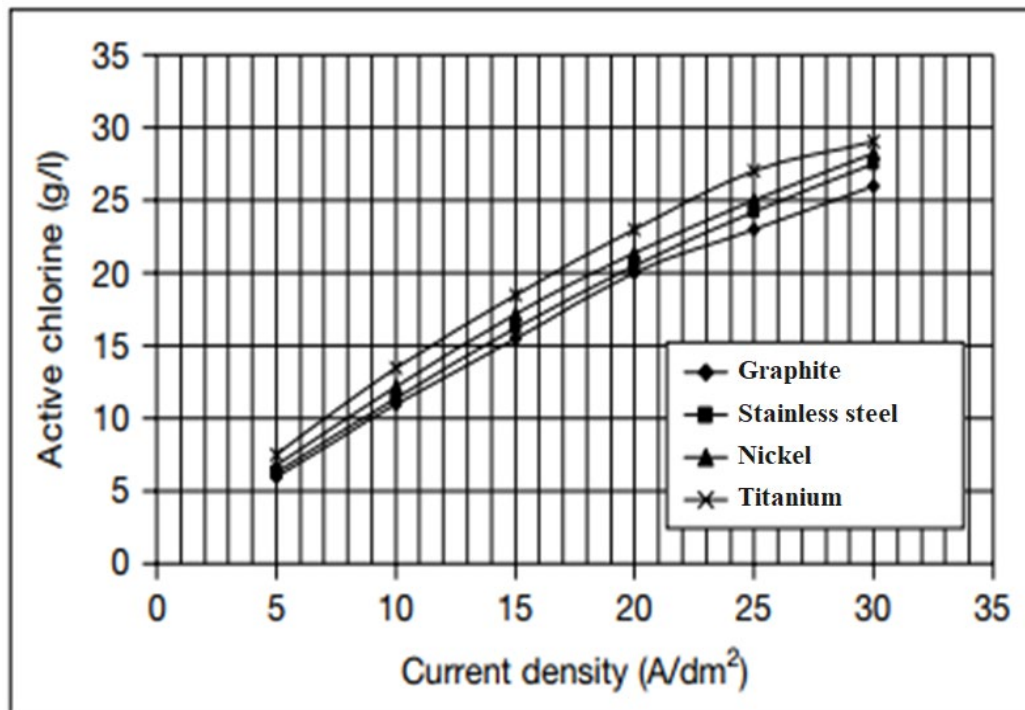


Figure 2.10: Effect of current density as a function of the type of the cathode [18].

Ti/TiRuO₂ anode; NaCl concentration 2M; Temperature 20°C; electrolysis time 1h.

Consequently, it is highlighted that the behavior of titanium is better than all others. Moreover, its resistance to corrosion avoids any type of pollution of the solution with metallic ions or graphite particles. However, the titanium cathode shows strong permeability to hydrogen. This generates very high mechanical tensions in its interior and causes its deformation. For this reason, cathodes of titanium coated with platinum (Ti/Pt) are preferred, or better yet with iridium oxide (Ti/IrO₂) [18].

2.3.5.6-Current Density

The electric current can be increased by increasing the salt concentration in the feed or the voltage between the electrodes, as well as by decreasing the distance between the electrodes [25].

The effect of the variation in active chlorine production as a function of the density of applied current for the anodes is illustrated in figure 2.11 [18]. Also, it should be known that when the current density increases there is also an increase in the cell temperature [30].

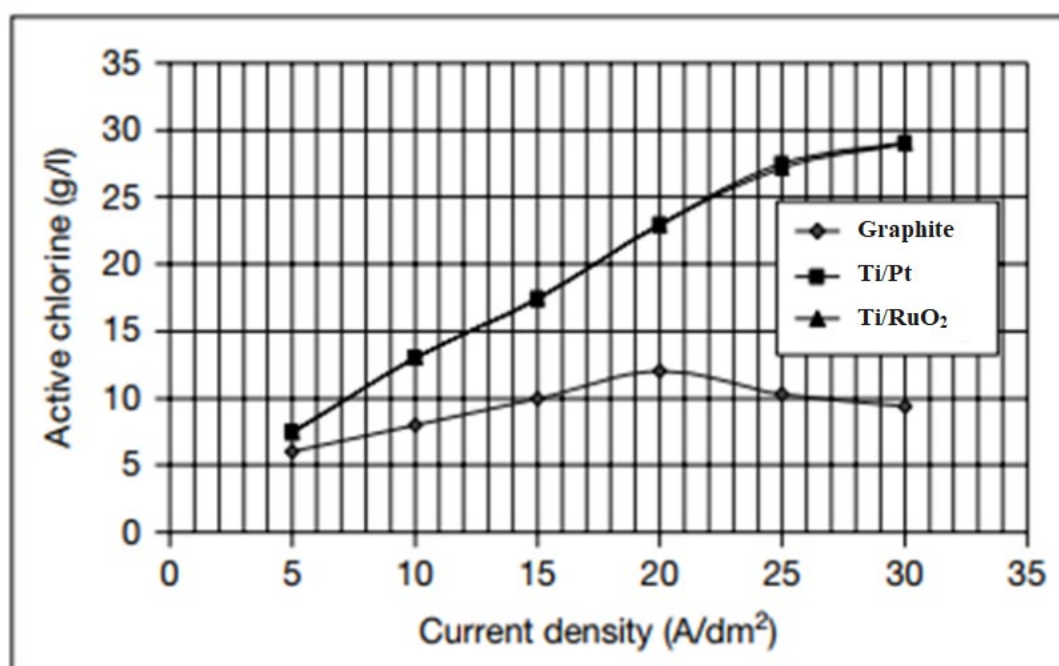


Figure 2.11: Effect of current density as a function of the nature of the anode [18].

Ti cathode; NaCl concentration 2M; temperature 20°C; electrolysis time 1h.

For the Ti/Pt and Ti/RuO₂ anodes, the AC increases almost linearly with increase of current density. a somewhat different tendency is observed for graphite anodes. In fact, AC increases up to a maximum of about 12 (g/l) at 20 (A/dm²); beyond this value, it diminishes

abruptly. The fact that the graphite anode could not tolerate a high current density can explain the phenomena observed. Beyond a current density of 20 (A/dm^2), reactions of chlorate formation and oxygen development take the upper hand. In contrast, Ti/Pt and Ti/RuO₂ anodes bear higher current densities without problems, and concentration of AC increases, even though with lesser yields [18].

2.3.5.7-Electrolysis Time

Figure 2.12 [18], indicates that the value of AC concentration increases in every case up to a maximum value and then decreases for prolonged periods. Indeed, for prolonged electrolysis times, the current flow drops, there is a strong development of oxygen, and transformation of Cl^- to ClO^- ions into ClO^- decreases, favoring the formation of chlorate. The behavioral superiority of Ti/RuO₂ anodes in comparison to other anodes is undeniable, in as much as it is possible to employ higher currents with less production of ClO_3^- . These results confirm that the best performances, in terms of producing active chlorine and efficiency of current, were given by the Ti/Pt and Ti/RuO₂ anodes. So, the criteria of choice of anode must take into account an important factor that influences the yield of the cell, i.e., the capacity to operate with long electrolysis times. While temperature does not have a very appreciable effect, current density, electrolyte concentration and electrolysis time are the parameters that most influence the parameters of the electro chlorination reaction [18].

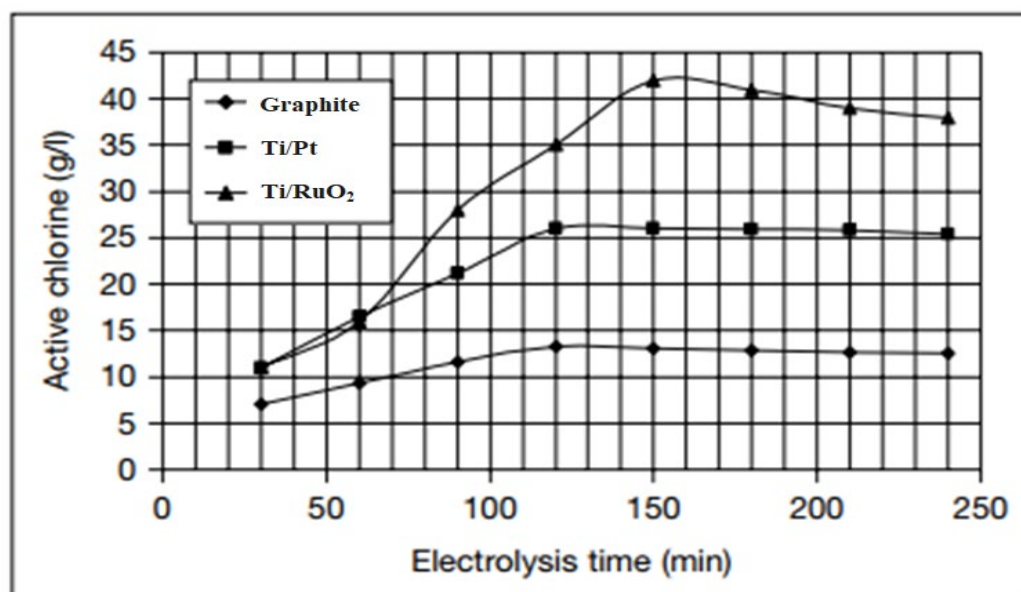


Figure 2.12: Effect of electrolysis time as a function of the nature of the anode [18].

Ti cathode; Sa/Sc = 1.33 cm; current density 15 A/dm^2 ; NaCl concentration 2M; Temperature 20°C.

2.3.5.8-Electrodes Geometry

Electrolytic cells may be designed having monopolar or bipolar electrode configurations. Each of these design configurations is discussed below.

A monopolar cell consists of an anode and cathode each joined to the power source by a separate power connection. These electrodes are separated by a space that allows the salt solution to flow between the plates for electrolysis to occur. Multiple electrodes may be connected to a common input connection in a parallel configuration within each electrolyzer assembly. Each electrode set polarity is defined by its connection polarity, anodes only on the positive connection and cathodes only on the negative connection. While the bipolar electrodes differ from those discussed above in that each electrode will serve as both an anode and a cathode. The bipolar cell design will have terminal electrodes for the positive and negative power input points and interstitial bipolar electrodes. Direct current is delivered to the positive DSA coated terminal electrode face, emitted from that electrode face through the brine solution, then is received on the cathode face of the adjacent plate and passes through the plate to the anode face of the same electrode. Each electrode has a DSA coated portion and a non-DSA coated portion. Current flow through the cell proceeds alternately through each bipolar electrode set in the cell to the non-DSA coated cathodic terminal electrode [11].

The form of the cell as well as the form and the geometrical arrangement of the electrodes are factors which can influence the process variables such as the flow rate and the hydrodynamics, the distance between the electrodes, the current density etc. Another consideration for choosing the form of the cell is the possibility for avoiding the occurrence of stagnant pockets of liquid in the cell which will enhance deposition of $Mg(OH)_2$ and $Ca(OH)_2$ on the surface of the cathode [25].

2.3.6-Control of The Parasite Reactions

When a salt (NaCl) solution is formed in water, sodium ions (Na^+) and chlorine ions (Cl^-) are produced according to the reaction [18]:



In the electrolytic cell, a potential difference is applied between the anode (+) and cathode (-), to generate reaction that led to the production of sodium hypochlorite. But due to impurities and some other parameters that has been mention above other reaction are

generated at the same time, that reduce the current efficiency which known as parasite reactions. Those side reaction or parasite reaction can't be eliminated, but it can be controlled by choosing the best operating condition [25]:

At the anode:



At the cathode:

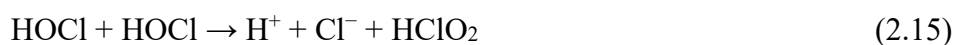


In the solution:



Reaction (2.14) is catalyzed by heavy metal ions, such as Fe and Cu ions, and is the principal reaction causing the dissociation of hypochlorite during storage. The formation of chlorate in the solution through (reaction 2.13) is favored by high temperature ($> 40^\circ\text{C}$) and low pH, because at low pH both HOCl and ClO^- are available in the solution. (reactions. 2.9 to 2.12) taking place at the electrode's surface are influenced by the operating conditions (concentration of NaCl, Voltage, solution flow rate) as well as by the electrodes material. Other side reactions causing a decrease of the current efficiency are those forming hydroxides from Mg and Ca ions ($\text{Mg}(\text{OH})_2$) and ($\text{Ca}(\text{OH})_2$) which take place in the surrounding of the cathode. The hydroxides will form a deposit on the surface of the cathode causing an increase of the over voltage and a decrease of the current efficiency [25].

There is other reaction like the hypochlorous in acidic solution:



Or hypochlorite in basic solution:



Or in a presence of UV source:



2.3.7-Cleaning Cycle

Finally, the cleaning cycle. Cell cleaning is an essential part for any process due to its great influence in the economy and safety sides. And with the proper cleaning of the cell, it helps to maintain a high efficiency, and help the cell maintain a long-life time, and prevent any critical failure which may lead to a disaster.

Salt and water contain calcareous material which reacts with the cathodic alkaline layer. Calcium and magnesium are the elemental materials that cause the deposits, the predominant deposit in on-site generation systems is calcium carbonate, these different deposits are caused by differences in the cell feed brine. Brine system feed has high calcium levels and essentially a somewhat neutral pH since drinking water is the source water. Although both deposit forms are easily removed by acid, the carbonate form in the on-site generation system is more quickly dissolved shortening the cleaning cycle.

Cell cleaning can be accomplished using either hydrochloric or sulfamic acid at a concentration ranging from 5 to 10 percent. Please note that cell cleaning must be performed on the schedule recommended by the electrochlorinator vendor to assure an adequate life from the electrolyzer cell system [31].

CHAPTER 3

SIZING

Chapter 3: Sizing

3.1-Overall Process Design

This chapter is concerned with sizing and designing an on-site sodium hypochlorite generation system with a concentration of 8 (g/l) that was detailed in the second chapter, for the sake of providing the daily needs of the disinfection process for drinking water in the TICHY-HAF dam. Taking into account the parameters that affect the overall process. It should be known that the design below is a flexible design that changes with the change of data.

This work is designed to provide a capacity of 40,000 cubic meters of drinking water per day, using approximately 44,500 cubic meters of raw water per day. The Figure 3.1 below is a simple design of the system equipment's arrangement. This Figure designed using EdrawMax software.

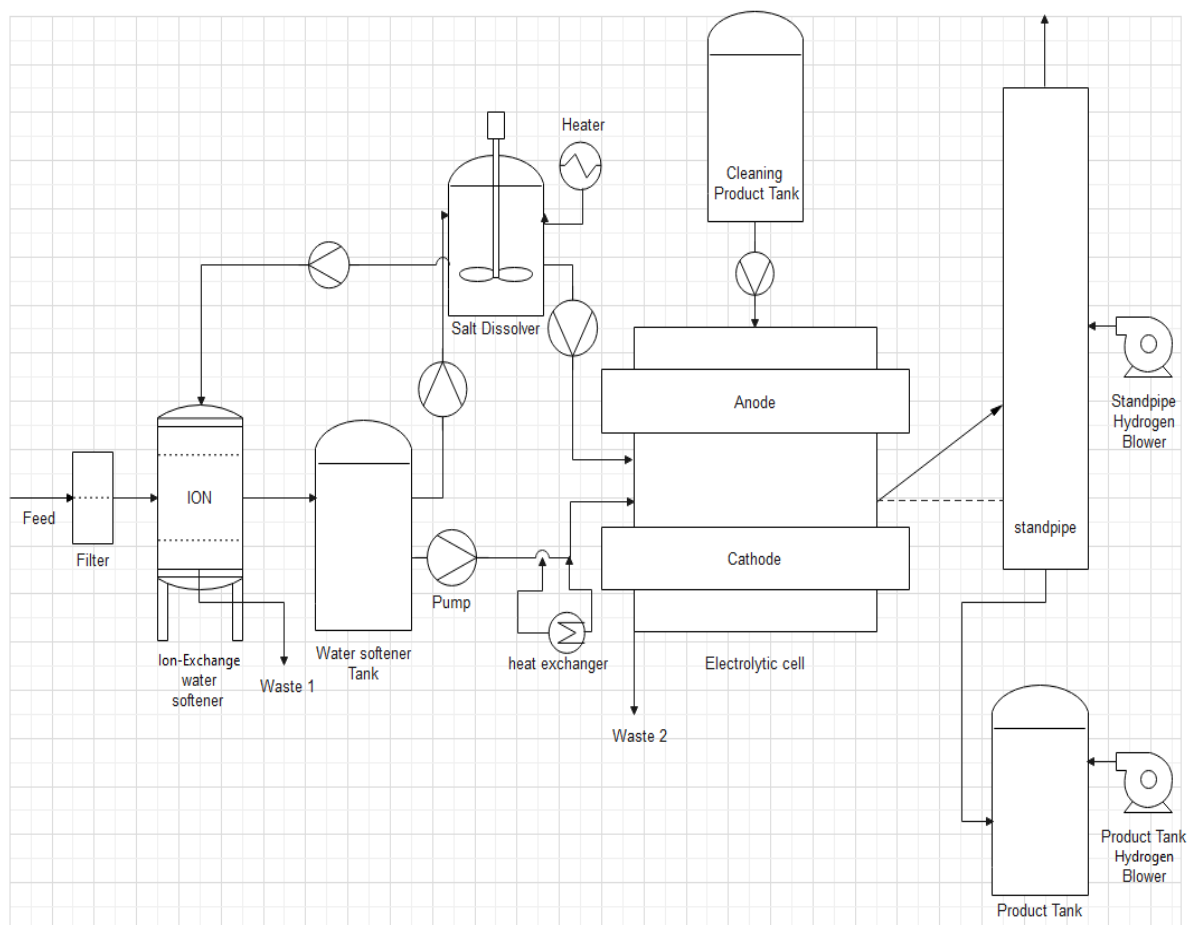


Figure 3.1: Typical on-site sodium hypochlorite system arrangement.

EdrawMax is a 2D business technical diagramming software which help create flowcharts, organizational charts, mind map, network diagrams, floor plans, workflow diagrams, business charts, and engineering diagrams.

3.2-Process Sizing

In this section both equipment capacity and raw material consumption will be sized. The results below were calculated according to the Water Hardness (TH) of 500 (mg/l), the concentration of sodium hypochlorite is 0.8% or 8 (kg/m³), while the dosage concentration they used is 0.005 and 0.003 (kg/m³) for pre-chlorination to the raw water, and post-chlorination to the treated water respectively.

You should know that an average dose of 0.001 to 0.005 (kg/m³) of sodium hypochlorite is the generally required for potable water. Wastewater dosing may vary up to 0.01 (kg/m³) [31].

3.2.1-Electrolytic Cell

With putting the cell design aside, the first equipment to be sized in the process is the electrolytic cell, and precisely the cell capacity of available chlorine/sodium hypochlorite production which calculated based on water treated every day, and the chlorination demand. For the TICHY-HAf project an electrolytic cell at least with a capacity of 343 kg of AC or 43 (m³) of sodium hypochlorite is needed every day in order to meet chlorination needs. the cell capacity is calculated based on the following formulas:

$$\dot{m}_{AC} = \dot{m}_{AC1} + \dot{m}_{AC2} \quad (3.1)$$

$$\dot{m}_{AC1} = \dot{V}_{raw} \times \dot{C}_{AC1} \quad (3.2)$$

$$\dot{m}_{AC2} = \dot{V}_{treated} \times \dot{C}_{AC2} \quad (3.3)$$

$$\dot{V}_{NaClO} = \dot{m}_{AC} / C_{AC} \quad (3.4)$$

With:

\dot{m}_{AC} : total mass flow rate of AC needed (kg/day) ;

\dot{m}_{AC1} : pre-chlorination mass flow rate of AC (kg/day) ;

\dot{m}_{AC2} : post-chlorination mass flow rate of AC (kg/day) ;

\dot{V}_{raw} : volumetric flow rate of raw feed water (m^3/day) ;

\dot{V}_{treated} : volumetric flow rate of treated feed water (m^3/day) ;

\dot{V}_{NaClO} : volumetric flow rate of sodium hypochlorite that used for disinfection (m^3/day) ;

\dot{C}_{AC1} : dosage concentration of AC used for raw water chlorination (kg/m^3) ;

\dot{C}_{AC2} : dosage concentration of AC used for treated water chlorination (kg/m^3) ;

C_{AC} : AC concentration which is 0.8% or 8 (kg/m^3).

The second thing to calculate about the electrolytic cell is the energy used each day, using the energy conversion efficiencies (ECE) which is provided by the electrolytic cell vendor. Typically, low-strength OSG systems require a 4.4 kWh of electricity per kg of available chlorine generated just for the electrolytic process of converting the brine solution to sodium hypochlorite [13]. the energy used for the process is 1510 (kWh) each day based on the following formula:

$$E_{\text{Cell}} = \text{ECE} \times \dot{m}_{\text{AC}} \quad (3.5)$$

With:

E_{cell} : the energy used by the electrolytic cell (kWh/day) ;

ECE : the energy used to convert brine solution to sodium hypochlorite (kWh/kg AC).

3.2.2-Salt Dissolver

Next the salt dissolver should be sized to provide the cell needs, and the water softener generation needs. The electrolytic cell work with a concentrated brine of 30 (kg/m^3) or (2.9% of salt in the brine solution), but a saturated brine solution is needed to prepared first in the salt dissolver, which is prepared with a concentration of 360 (kg/m^3) or (26.47% of salt in the brine solution) at 20°C based on [32]. In this work, we will use a concentration of 358 (kg/m^3) to prepare the brine solution, this concentrated solution is then diluted before entering the cell or when entering, also the brine density is needed which is 1200.23 (kg/m^3) at 20°C [33]. You should know that the salt concentration of salt used in the preparing of the brine solution is high to achieve the saturation, but the concentration that used in process may drop to 300 (g/l).

The salt conversion is needed to calculate the dissolver capacity, the salt, and the water needed for the saturated brine solution. The salt conversion is provided by the electrolytic cell vendor, in this work a salt conversion of 3.5 (kg salt/kg AC) [12], will be used.

Based on the information above a brine solution flow rate of 4.36 m³ is needed every day to provide the cell needs, with a consummation of 1201 kg of salt and 3.36 m³ of softened water each day. The following formulas are used in the calculation:

$$\dot{m}_{\text{salt1}} = \dot{m}_{\text{AC}} \times Z_{\text{SC}} \quad (3.6)$$

$$\dot{V}_{\text{WB}} = \dot{m}_{\text{salt1}} / \dot{C}_{\text{BS}} \quad (3.7)$$

$$\dot{V}_{\text{BS}} = (\dot{m}_{\text{salt1}} / \rho_{\text{b}}) + \dot{V}_{\text{WB}} \quad (3.8)$$

With:

\dot{m}_{salt1} : salt used on sodium hypochlorite production (kg/day) ;

Z_{SC} : salt conversion of sodium hypochlorite to AC (kg salt/kg AC) ;

\dot{V}_{WB} : volumetric flow rate of softened water needed for brine solution that used in sodium hypochlorite production (m³/day) ;

\dot{C}_{BS} : salt concentration in brine solution (kg/m³) ;

\dot{V}_{BS} : volumetric flow rate of brine solution that used in the sodium hypochlorite production (m³/day) ;

ρ_{b} : brine density (kg/m³).

While the salt consumption for the generation of water softener based on the (equations 3.12 to 3.16, and 3.9) is 97.5 (kg) of salt for every regeneration, and 0.2724 (m³) of softened water for the brine solution that used in the regeneration. Finally, the total volume of brine solution is 4.72 (m³/day) based on the (equation 3.11):

$$\dot{V}_{\text{WBR}} = \dot{m}_{\text{salt2}} / \dot{C}_{\text{BS}} \quad (3.9)$$

$$\dot{m}_{\text{salt}} = \dot{m}_{\text{salt1}} + \dot{m}_{\text{salt2}} \quad (3.10)$$

$$\dot{V}_{\text{BT}} = (\dot{m}_{\text{salt}} / \rho_{\text{b}}) + \dot{V}_{\text{WB}} + \dot{V}_{\text{WBR}} \quad (3.11)$$

With:

\dot{V}_{WBR} : volumetric flow rate of softened water needed for preparing brine solution that used in water softener regeneration (m^3/day) ;

\dot{m}_{salt2} : salt used for water softener regeneration (kg/day) ;

\dot{m}_{salt} : total salt used in the process (kg/day) ;

\dot{V}_{BT} : total volumetric flow rate of brine solution used for sodium hypochlorite production and regeneration of water softener (m^3/day).

now the salt dissolver size is depending on some parameters like the budget and the space you can provide, for example a 5 (m^3) dissolver can provide the needed brine, with a recharge one time in a day. But although the dissolver can handle the brine supply for a full day it is not recommended to regenerate the dissolver one time per day, due to the unknown time of the regeneration which may affect the production. While the salt tank is recommended to handle a storage for long time, for example you need a tank storage of about 10 tons to handle a week supply, which can be considered good for this level of production.

3.2.3-Water Softener:

As has been discussed in the second chapter about the effect of the purity, and hardness of the water, the water softener like a sodium zeolite softening work with exchange ion, between sodium ions and calcium, magnesium ions, when the raw water enters the softener, it passes by a resin bed that containing what is known as Strong Acid Cation (SAC) resin in the sodium form, the hardness ions are exchanged with the sodium to give us a free hardness water which is known as soft water [34]. That is what make the water softener so important for this process.

In this section a water softener will be sized to provide the water needed for the saturated brine, and for the dilution of this brine solution, so the cell can work with a brine concentration of 30 (kg/m^3).

Now before we figure out the capacity of the softener and the amount of resin needed, we need some information about our water hardness, and the regeneration effectiveness of resin using brine solution which needed to provide by the vendor. As a start the water hardness in the TICHY-HAF dam is about 500 (mg/l), next we need to find the resin volume

which we can calculate from (equation 3.15), and resin exchange capacity (\dot{M}_R) this capacity change depends on the technology we use and the salt dosage in the generation, the Figure 3.2 shown the change of capacity and efficiency with the change of salt dosage [35], in this work we will use a salt dosage of about 15 (lb/ft³ resin) which is 240.3 (kg/m³ resin) in the SI units, and with a resin exchange capacity of 30000 (grains/ft³ resin) which is about 1059440 (grains/m³ resin).

And at last, the water needed for the regeneration including; backwash, brine draw, slow rinse, and fast rinse. This process took up to an hour and a half, and a total volume of about 4 m³ of water for each generation [36].

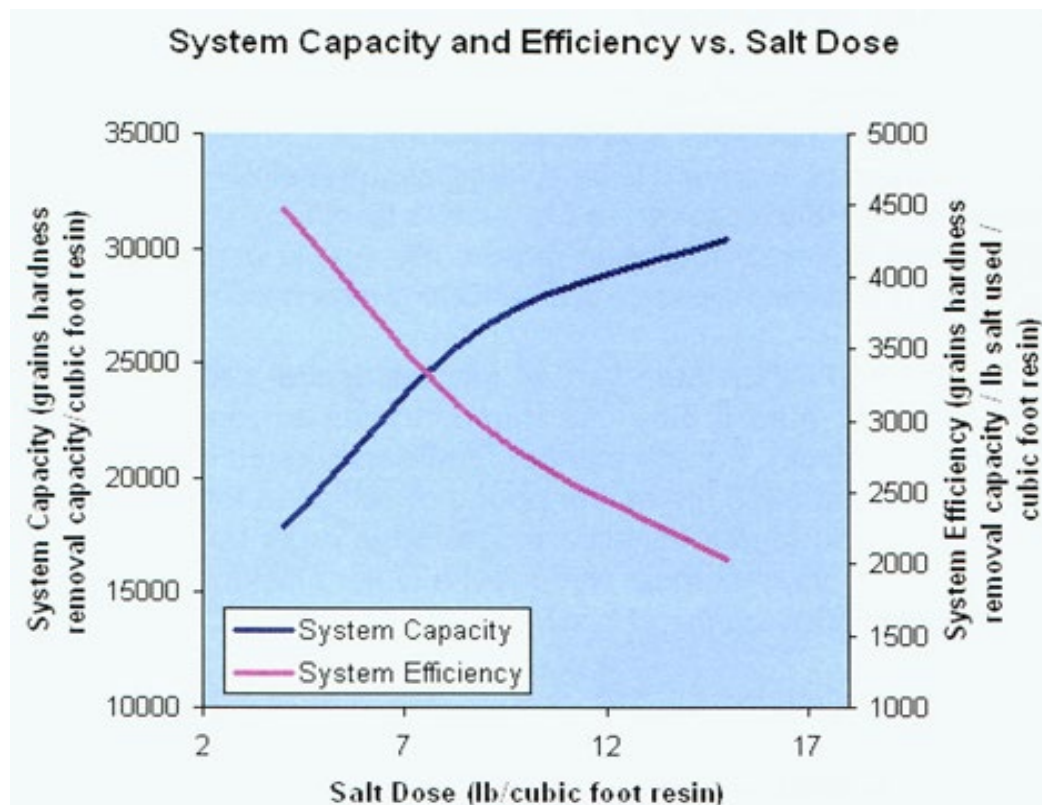


Figure 3.2: the change of the resin exchange capacity and efficiency with the change of salt dosage [35].

A softener with a capacity of at least 0.4054 (m³) of resin, so the softener can generate about 55.7 (m³) of softened water each day. Now if you want to use only one softener with regeneration one time every day you need to rise the softener capacity so the process will keep working in the regeneration time which is about 2 hours, we can calculate the new capacity by changing (\dot{V}_{WT}) with (\dot{V}_{WTR}). The final capacity (\dot{V}_{RR}) is 0.45 (m³) of resin so

the water softener can do a work of a day in 22 hours and the other 2 hours is for the generation. The following formulas are used in the calculation:

$$\dot{V}_{WT} = \dot{V}_{WB} + \dot{V}_{WD} + \dot{V}_{WBR} \quad (3.12)$$

$$\dot{V}_{BS} \times \dot{C}_{BS} = \dot{V}_{WD} \times \dot{C}_{DS} \quad (3.13)$$

$$\Rightarrow \dot{V}_{WD} = \dot{V}_{BS} \times \dot{C}_{BS} / \dot{C}_{DS}$$

$$\dot{G}_S = \dot{V}_{WT} \times TH \quad (3.14)$$

$$\dot{V}_R = \dot{G}_S / \dot{M}_R \quad (3.15)$$

$$\dot{m}_{\text{salt}2} = \dot{V}_R \times Z_{\text{SDR}} \quad (3.16)$$

$$\dot{V}_{WTR} = \dot{V}_{WT} + (\dot{V}_{WT} \times 2 / 24) \quad (3.17)$$

With:

\dot{V}_{WT} : total volumetric flow rate of softened water needed for sodium hypochlorite production (m^3/day) ;

\dot{V}_{WD} : volumetric flow rate of water needed for brine dilution (m^3/day) ;

\dot{C}_{DS} : salt concentration in the diluted solution (kg/m^3) ;

\dot{G}_S : grain that should be removed by the water softener (grains/day) ;

TH : total hardness (grains/m^3) ;

\dot{M}_R : resin exchange capacity (grains/m^3 resin) ;

\dot{V}_R : Resin volume used to remove the total hardness (m^3 resin /day) ;

Z_{SDR} : salt dosage conversion of water softener regeneration ($\text{kg salt}/\text{m}^3$ resin) ;

\dot{V}_{WTR} : total volumetric flow rate of softened water needed for sodium hypochlorite production including regeneration time (m^3/day);

\dot{V}_{RR} : Resin volume used to remove the total hardness including regeneration time (m^3 resin/day).

The total flow rate of both water and brine solution entering the electrolytic cell is about 56.5 cubic meters that used for the production every day.

$$\dot{V}_T = \dot{V}_{WD} + \dot{V}_{BS} \quad (3.18)$$

With:

\dot{V}_T : The total volumetric flow rate of the solution that enter the cell for sodium hypochlorite production (m^3/day).

A storage tank with a capacity of 9 (m^3) to handle the water needed for the brine solution and about two hours of water that used for the dilution of brine solution, to maintain the supply even in the regeneration time. also, a microfilter is recommended to be installed before the water softener to prevent insoluble substances like sand from entering the softener. And the softener has to withstand the flow rate required by the process.

The sizing above is flexible and can change depending on the various needs, for example, you can use two water softeners so you can reduce the capacity of the storage tank. Also, the softener sizing can change depending on the salt dosage.

3.2.4-water heater and water chiller:

The temperature has an important effect especially on the brine preparation and the sodium hypochlorite production, this is why there is a need for a heater/chiller depending on the temperature in the field, also you should know that besides the natural temperature of the area, some of the equipment can raise the overall temperature like the electrolytic cell, and the blower. and depends on those factors the engineer can decide if he needs a heater or a cooler system. Also, a tank heater is recommended in the dissolver to maintain a temperature above 20°C , as we mentioned above that we work with a concentration of $358 \text{ (kg/m}^3\text{)}$ of sodium chloride, and this solubility achieved at a temperature of 20°C .

3.2.5-Hydrogen treatment:

Beside the production of sodium hypochlorite, the hydrogen also is generated based on the (reactions. 2.3 and 2.4) at a huge quantity, and due to its flammability and explosiveness a special treatment is needed for safety. As a safety measure, the system is designed to maintain the hydrogen gas concentration in air below 25% of the Lower Explosive Limit (LEL, or 1% by volume, also a safety factor (SF) of 4 is recommended. The hydrogen gas is formed in the electrolytic cells at a stoichiometric rate of approximately 0.04 kg of hydrogen per 1 kg of AC [12].

For the design safety some provide a standpipe with a blower to separate and dilute the hydrogen before vented to atmosphere, and the sodium hypochlorite solution goes to the storage tank, also it is recommended to installed a blower in the storage tank for safety. And there is some who dilute hydrogen directly from storage tank without using a standpipe. The design in this work is provided with a standpipe.

The principle governing the design of a hydrogen dilution standpipe is that of mass and concentration differential. As the two-phase flow exits the OSG chamber, the hydrogen gas concentration in the solution and at the solution surface is higher than that in the surrounding air. The blowers force air to the surface of the liquid and dilute the hydrogen before it is vented to the atmosphere. The dilution standpipe is an open, vertical, cylindrical pipe that is located between the electrolytic cells and the sodium hypochlorite storage tank. 0.9-meter diameter is enough for a system with more than 600 (kg AC/day). Also, it is recommended that the standpipe be placed within a two meters radius from the electrolytic cells to minimize hydraulic backpressure. The electrolytic cell discharge pipe should have an upward slope of at least 21 (mm/m) (or 1.2°) toward the standpipe. The vent stack of the standpipe should extend at least one meter above the highest point of the building housing the standpipe, and the highest point in any building within six meters from the vent stack. Also, the blower inlet should be above the solution inlet that come from the cell with about 8 centimetres [12].

The blower is sized on the maximum hydrogen production. A 65000 (m³/day) flow rate of air is needed to dilute the hydrogen that produced each day which is about 14 (kg). The following formulas are used in the calculation:

$$\dot{m}_{H_2} = \dot{m}_{AC} \times F_{H_2} \quad (3.19)$$

$$\dot{N}_{H_2} = \dot{m}_{H_2} / M_{H_2} \quad (3.20)$$

$$\dot{N}_{air} = \dot{N}_{H_2} \times (1 \text{ mol air} / 0.01 \text{ mol } H_2) \times SF \quad (3.21)$$

(1% of hydrogen equal 1-part air / 0.01-part H₂)

$$Q_{air} = \dot{N}_{air} \times R \times T_{air.STD} / P_{air} \quad (3.22)$$

With:

\dot{m}_{H_2} : mass flow rate of hydrogen that generated in the cell (kg/day) ;

F_{H_2} : hydrogen production factor (kg H₂/kg AC) ;

\dot{N}_{H_2} : molar flow rate of hydrogen (mol/day) ;

M_{H_2} : mass molar of hydrogen (kg/mol) ;

\dot{N}_{air} : molar flow rate of air (mol/day) ;

Q_{air} : air volumetric flow rate (m³/day) ;

R : universal gas constant (m³×atm/°K×mol) ;

$T_{air.STD}$: standard air temperature (°K) ;

P_{air} : air pressure (atm).

The standpipe blower needed to be sized to provide 65000 m³ of air every day, while the tank storage blower is sized to provide half of the daily air dilution volumes, the power required for the blower to move this air volume for hydrogen dilution can be calculated using (equation 3.24). But I can't calculate it due to the lack of the static pressure (P_{st}) which I found that it is typically measured using pressure gauges that attached to the side of a pipe. The following formulas are used in the calculation [12].

$$\dot{W}_{th} = Q_{air} \times P_{total} \quad (3.23)$$

$$\dot{W}_{real} = \dot{W}_{th} / \eta_b \quad (3.24)$$

$$V_{air} = Q_{air} / OA \quad (3.25)$$

$$OA = \pi r_{dp}^2 / \sin(\text{angle of the pipe}^\circ) \quad (3.26)$$

$$P_{total} = P_{st} \times P_{dyn} \quad (3.27)$$

$$P_{dyn} = (1/2) \times \rho_{air} \times V_{air} \quad (3.28)$$

With:

\dot{W}_{th} : is the theoretical power required to move a given air volume against a given pressure (w);

\dot{W}_{real} : is the real power required to move a given air volume against a given pressure (w) ;

η_b : efficiency of blower ;

v_{air} : air velocity (m/day) ;

OA : discharge pipe cross-sectional area (m^2) ;

r_{dp} : discharge pipe radius (m) ;

π : pi number or Archimedes' constant ;

P_{total} : total pressure or stagnation pressure (Pa) ;

P_{dyn} : dynamic pressure (Pa) ;

P_{st} : static pressure (Pa).

3.2.6-Storage tank:

The sodium hypochlorite that's coming out of the standpipe goes directly to the storage tank. Usually, the storage tank designed to handle about a day of the sodium hypochlorite demand, which is in our situation we need a tank that can handle a 43 (m^3). But this system is designed to provide only the daily demand which mean all the generated sodium hypochlorite is directly used in the disinfection process. And so, a tank of about two cubic meters is enough to store the product before the dosage.

The dosage in system like this is generally achieved using positive displacement pumps to overcome system dosing point pressures. Variable speed drive controls are commonly used to assure the correct dosage [11].

3.2.7-pipes and pumps sizing:

Before sizing the pumps, the pipeline's sizes should be known, like the diameter, the total length and shape, and the material of the pipelines.

The pipeline's material is chosen depending on the effect of the liquid-like corrosivity, and the pipe material will affect the calculation due the roughness change from one material to another.

Next, the total length and shape of pipes are sized according to the available space on the production line, the equipment sizes, and taking into consideration some equipment like the standpipe should be placed within two meters from the electrolytic cell. All these parameters will affect the pressure drop across the system.

Finally, the diameter of pipes, which it also has a huge effect on the pressure drop, the fluid velocity, and the overall process costs. The pipe's diameter can be calculated with the help of (Equation 3.31), depending on the liquid flow rate, and the liquid velocity. The velocity used here is 2.25 (m/s).

$$\dot{V}_{\text{liquid}} = v_{\text{liquid}} \times A \quad (3.29)$$

$$A = \pi \times D_{\text{pipe}}^2 / 4 \quad (3.30)$$

$$D_{\text{Pipe}} = \sqrt{4V / \pi \times v} \quad (3.31)$$

With:

\dot{V}_{liquid} : liquid volumetric flow rate (m³/day) ;

v_{liquid} : liquid velocity (m/s) ;

A : pipe area (m²) ;

D_{Pipe} : Pipe diameter (m).

The following diameters are based on the flow rates calculated before:

The pipeline between the softener and the tank softener is with a diameter of 20(mm), a pump needed to be sized to provide a water flow rate of 61 (m³/day) from the dam to the softener tank passing by the filter and the water softener.

The pipeline between the softener tank and the salt dissolver is with a diameter of 10(mm), a pump needed to be sized to provide a 4 (m³) of softened water to the dissolver, this volume is delivered one time in a day if you work with a one-time regeneration system.

The pipeline between the dissolver and the electrolytic cell is with a diameter of 10(mm), a pump needed to be sized to provide a 4.5 (m³/day) of brine solution to the electrolytic cell.

The pipeline between the softener tank and the electrolytic tank is with a diameter of 19 (mm), a pump needed to be sized to provide a 52.5 (m³/day) and of softened water to the electrolytic cell.

The pipeline between the electrolytic cell and the standpipe is with a diameter of 17 (mm), no pump is needed due the high pressure inside the electrolytic cell.

3.3-Instruments System

System instruments are designed to provide continuous monitoring so the system operates within the acceptable operating limits. Systems from all vendors will have the same general alarm and status indicators to confirm proper operation, each of these alarm situations will shut down system operations to prevent serious damage to the equipment or hazard to the personnel. All electrolysis systems are designed to have the all or some of the following [11, 12]:

- water and brine flow indication: Water and brine flow meters are essential to confirm a generally accepted water to brine ratio of (12:1).

- cell level sensors, and alarms: Cell operation is prevented during filling at start-up and after acid cleaning. This lockout mode assures that the electrodes are always covered by brine solution. Actions as closing the cell discharge valve should immediately stop cell electrolysis to prevent any damage to the cell.

- cell temperature sensors, and alarms: Flow alarms are required to be certain that the cell temperature does not exceed 60°C or cell damage will occur. The addition of a temperature sensor is part of a comprehensive safety system to stop cell electrolysis should the flow sensor fail.

- tank level indication, and alarms: Tank level instruments are designed to operate the system when refilling the tank is necessary, to protect the dosing pumps, and prevent tank overflow. Generally, two operating set points and two alarm points are used for tank level instruments. The operating set points maintain the tank level by operating the system. The low-level alarm set point will stop the pumps and alarm while maintaining generator operation.

- dosing point residual indication: dosing flow meters are necessary to confirm the necessary dose of sodium hypochlorite at chlorination sites.

- hydrogen sensors, and alarms: An alarm system should be installed in the room to monitor the hydrogen concentration. The system should consist of one hydrogen transmitter with at least two independent sensors. Upon high hydrogen alarm, the system will shut down,

and a high-rate ventilation system is energized, the ventilation should be sized to dilute the maximum hydrogen production and operates for at least 10 min after the hydrogen alarm stops.

CONCLUSION

Conclusion

The objective of this dissertation is Sizing and Optimization of In-Situ Electrolysis Process Generator of Sodium Hypochlorite for Drinking Water Treatment Plant of the TICHY-HAF Dam

An electrolyzer is sized in this work with the other equipment to provide the disinfectant needs according to the drinkable water consumption.

The minimum volumetric flow rate of sodium hypochlorite needed for the disinfection process in the TICHY-HAF dam is found to be 43 (m³/day) with concentration of 8 (g/l).

Sodium hypochlorite production is achieved by converting the diluted brine solution in the electrolyzer using a direct current. A total of 56.5 (m³/day) of diluted brine solution, and 1510 (kWh) of energy used each day to provide the disinfectant needs.

As a perspective, and a continuation of this work, I recommend a study on the water of the TICHY-HAF dam to calculate the precise dosage, the contact time, and to sizing a contact tank to improve the effectiveness of disinfection.

Finally, I would like to point out the challenge that facing Algeria in the matter of managing water resources, especially with the increase in consumption and the impact of global warming, which calls for thinking about alternative solutions while carrying out campaigns to rationalize the use of water.

APPENDICES

Appendix A:

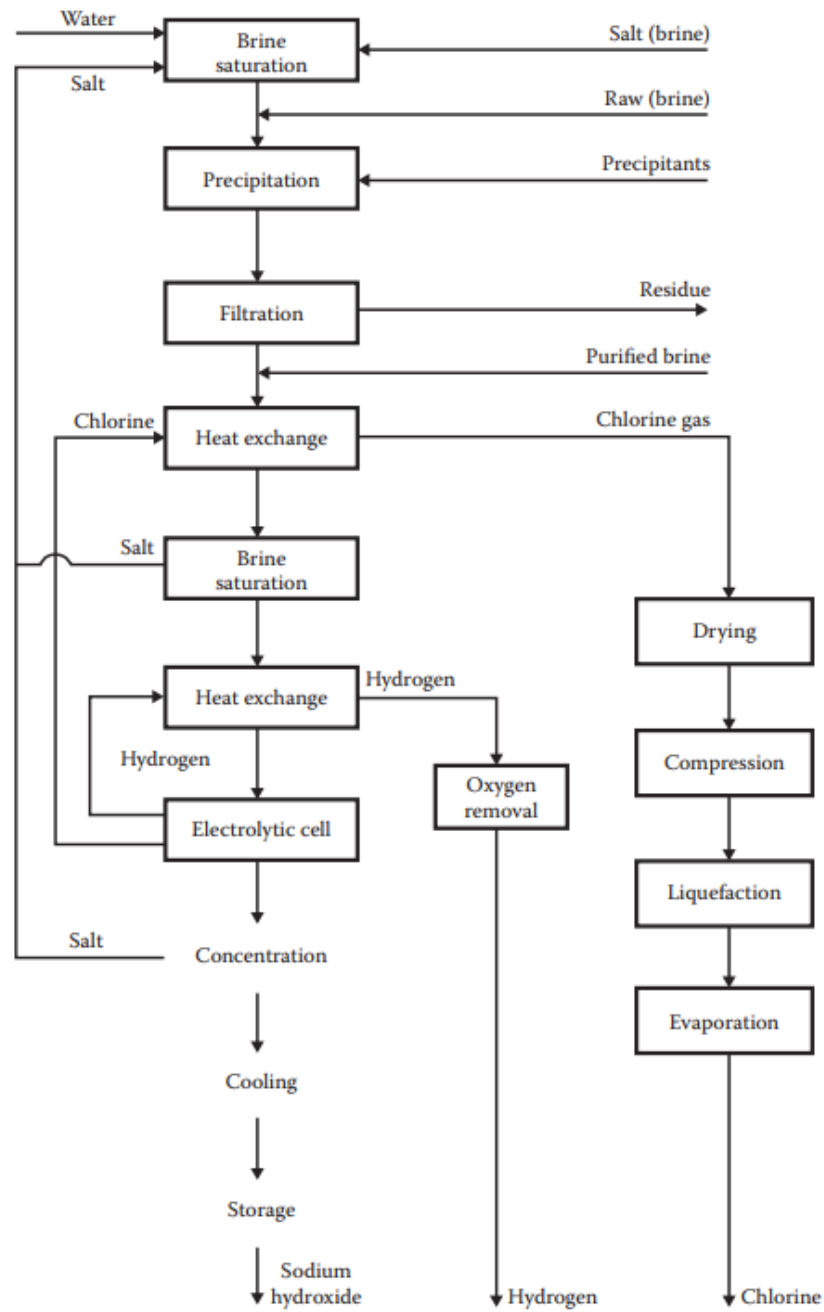


Figure A1: Diaphragm cell process flow [3].

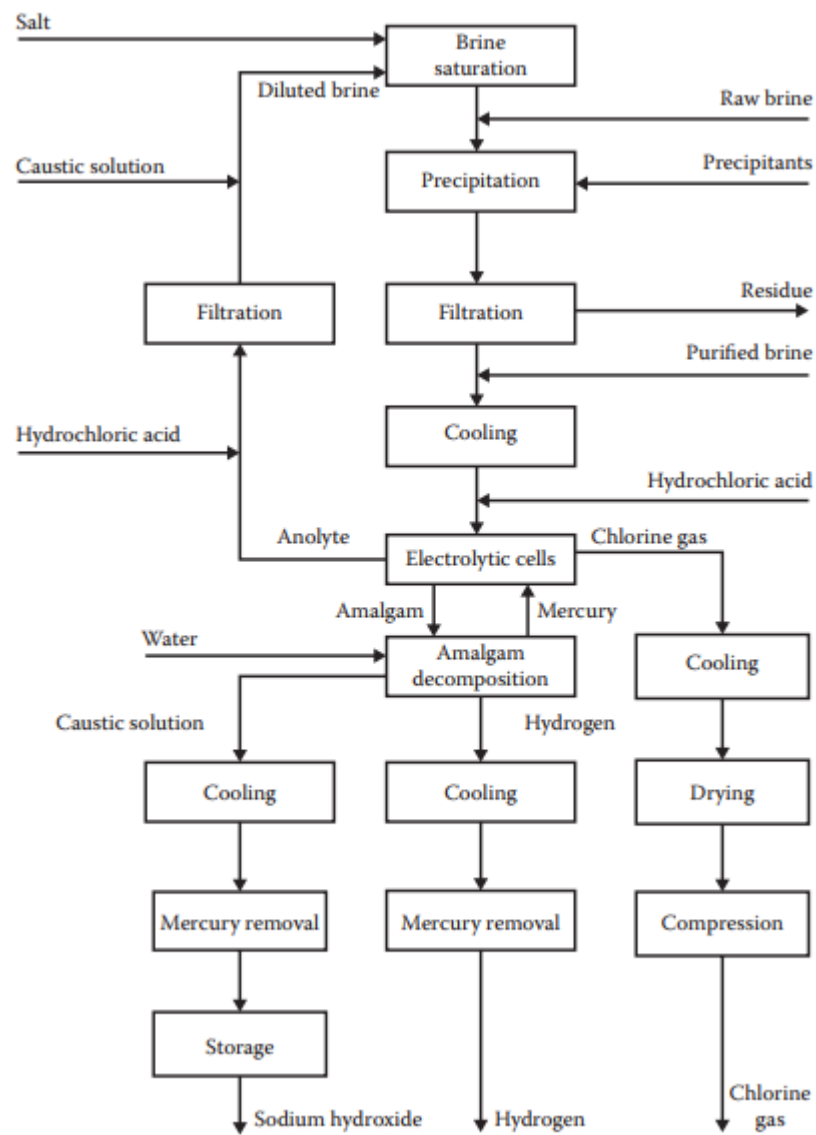


Figure A2: Mercury cell process flow [3].

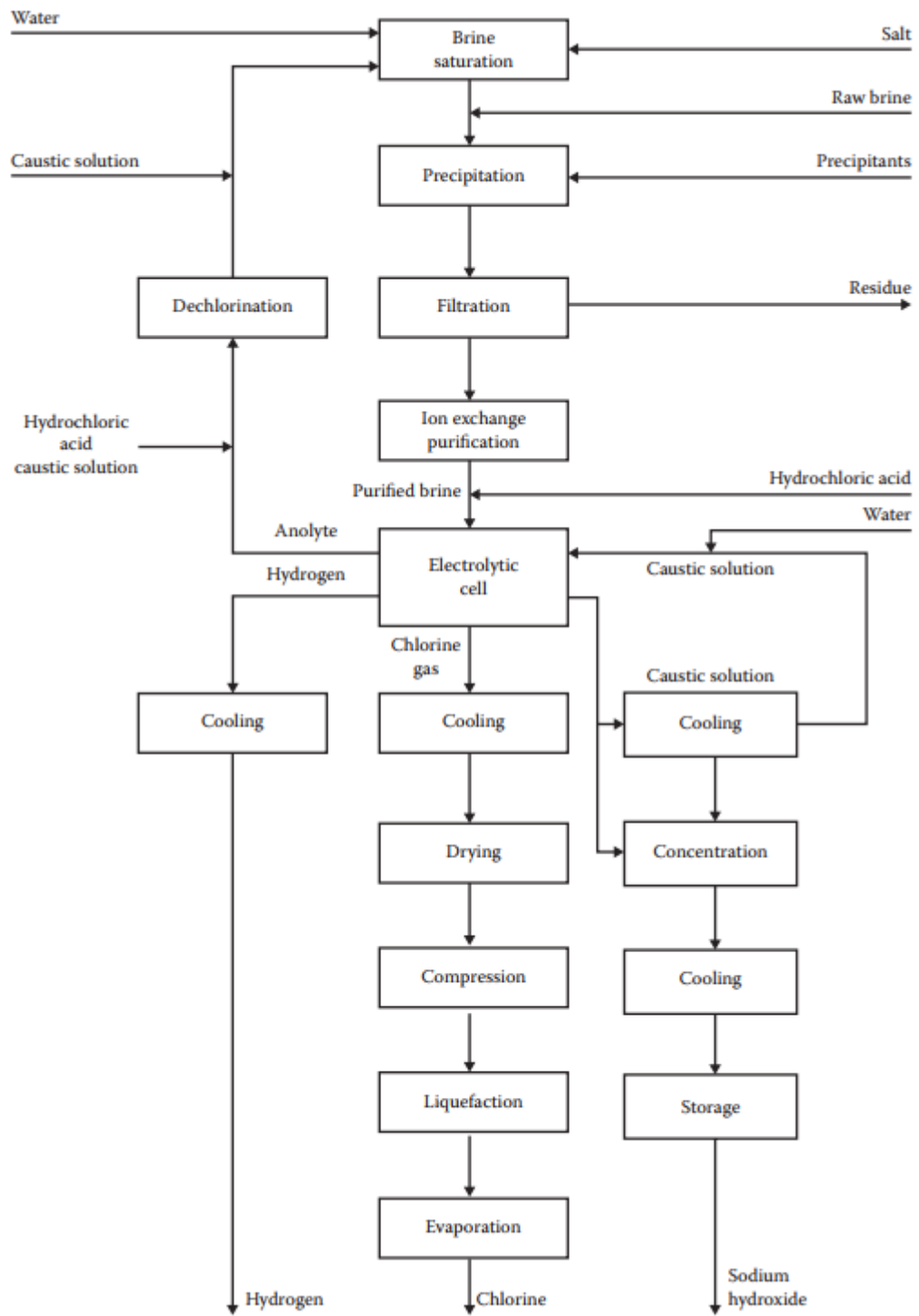


Figure A3: Membrane cell process flow [3].

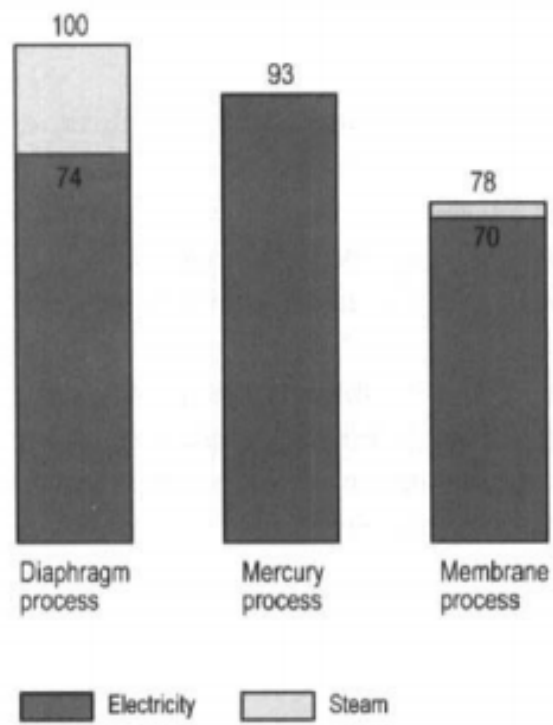


Figure A4: Relative consumption of energy (electricity and steam) in the three chlor-alkali processes in producing 50 wt% NaOH [20].

Appendix B:

Table B1: Main Water Treatment Categories and Unit Processes Listed in Order of Use [15].

Treatment Category	Unit Process
<i>Intake</i>	
Pre-treatment	Coarse screening
	Pumping
	Storage
	Fine screening
	Equalization
	Neutralization
	Aeration
	Chemical pre-treatment
Primary treatment	Coagulation
	Flocculation
	Sedimentation
Secondary treatment	Rapid sand filtration
	Slow sand filtration
Disinfection	Disinfection
Advanced treatment	Adsorption
	Activated carbon
	Fe and Mn removal
	Membrane processes
Fluoridation	Fluoridation
Distribution	

Table B2: the variation of hypochlorous Acid with pH and Temperature as variables [15].

pH	HOCl (%)						
	0°C	5°C	10°C	15°C	20°C	25°C	30°C
6.0	98.5	98.3	98.0	97.7	97.4	97.2	96.9
6.5	95.5	94.7	94.0	93.2	92.4	91.6	91.0
7.0	87.0	85.1	83.1	81.2	79.3	77.5	75.9
7.5	68.0	64.3	60.9	57.7	54.8	52.2	49.9
8.0	40.2	36.3	33.0	30.1	27.7	25.6	23.9
8.5	17.5	15.3	13.5	12.0	10.8	9.8	9.1
9.0	6.3	5.4	4.7	4.1	3.7	3.3	3.0

Table B3: Median concentrations of organic disinfectant by-products in drinking-water [37].

DBPs	Median concentration (: g/litre): chlorination ^a
THMs	40
Chloroform	15
BDCM	10
DBCM	4.5
Bromoform	0.57
HANs	2.5
TCAN	<0.012
DCAN	1.1
BCAN	0.58
DBAN	0.48
Haloketones	0.94
DCPN	0.46
TCPN	0.35
HAAs	20
MCA	1.2
DCA	6.8
TCA	5.8
MBA	<0.5
DBA	1.5
Aldehydes	7.8
Formaldehyde	5.1
Acetaldehyde	2.7
Glyoxal	–
Methylglyoxal	–
Chloral hydrate	3.0
Ketoacids	–
Trichlorophenol	<0.4

Table B4: Main typical characteristics of the different electrolysis techniques [38].

Criterion	Mercury	Diaphragm	Membrane
Anode	RuO ₂ + TiO ₂ coating on Ti substrate	RuO ₂ + TiO ₂ + SnO ₂ coating on Ti substrate	RuO ₂ + IrO ₂ + TiO ₂ coating on Ti substrate
Cathode	Mercury	Steel (or steel coated with activated nickel)	Nickel coated with high area nickel-based or noble metal-based coatings
Separator	None	Asbestos, polymer-modified asbestos, or non-asbestos diaphragm	Ion-exchange membrane
Cell voltage	3.15–4.80 V	2.90–3.60 V	2.35–4.00 V
Current density	2.2–14.5 kA/m ²	0.8–2.7 kA/m ²	1.0–6.5 kA/m ²
Temperature	Inlet: 50–75 °C Outlet: 80–90 °C	NI	NI
pH	2–5	2.5–3.5	2–4
Cathode product	Sodium amalgam (Na-Hg _n)	10–12 wt-% NaOH and H ₂	30–33 wt-% NaOH and H ₂
Decomposer product	50 wt-% NaOH and H ₂	No decomposer needed	No decomposer needed
Evaporator product	No evaporation needed	50 wt-% NaOH	50 wt-% NaOH
Quality of caustic soda (50 wt-% NaOH)	NaCl: ~ 50 mg/kg NaClO ₃ : ~ 5 mg/kg Hg: ~ 0.1 mg/kg	NaCl: ~ 10 000 mg/kg (15 000–17 000 mg/kg before concentration) NaClO ₃ : ~ 1 000 mg/kg (400–500 mg/kg before concentration)	NaCl: ~ 50 mg/kg NaClO ₃ : ≤ 10–50 mg/kg
Chlorine quality	O ₂ : 0.1–0.3 vol-% H ₂ : 0.1–0.5 vol-% N ₂ : 0.2–0.5 vol-%	O ₂ : 0.5–2.0 vol-% H ₂ : 0.1–0.5 vol-% N ₂ : 1.0–3.0 vol-%	O ₂ : 0.5–2.0 vol-% H ₂ : 0.03–0.3 vol-%
Advantages	50 wt-% high-purity caustic directly from cell, high-purity chlorine and hydrogen, simple brine purification	Low quality requirements of brine, low electrical energy consumption	Low total energy consumption, low investment and operating costs, no use of mercury or asbestos, high-purity caustic, further improvements expected
Disadvantages	Use of mercury, expensive cell operation, costly environmental protection, large floor space	High steam consumption for caustic concentration in expensive multi-effect evaporators, low-purity caustic, low chlorine quality, some cells are operated with asbestos diaphragms	High-purity brine required, low chlorine quality, high cost of membranes

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