STUDY OF HYPOCHLORITE PRODUCTION IN AN ELECTROLYTIC CELL

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ABSTRACT

Hypochlorite is employed as a disinfectant, powerful oxidizing agent and deodorant in dairies, creameries, water supplies, sewage disposal and for house hold purposes. It is not only stronger oxidizing agent than chlorine but is much more reactive and can bleach more rapidly at room temperature. Hypochlorite has drawn our attention because of its wide application and can be produced from sodium chloride which is easily available in Bangladesh.

An electrochemical cell system was devised using graphite anode and stainless steel cathode for the production of hypochlorite by the electrolysis of sodium chloride solution. The experiments were performed normally with 4.0M sodium chloride solution and in some cases potassium dichromate was added to increase the hypochlorite production. The operating current density was varied from 187.5 Am^{-2} to 750 Am^{-2} and pH between 6 to 10 at room temperature.

The performance of this cell for hypochlorite production was assessed in terms of current efficiency, power consumption and space time yield. The maximum current efficiency obtained in this investigation was 90.70% at current density 625 Am^{-2}. The minimum power consumption was found to be 6882.66 KWhr/ton for hypochlorite production and space time yield was also satisfactory in this case. A comparison has been made with the studies of other workers and the present cell was found satisfactory.

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CONTENTS

CHAPTER 1 INTRODUCTION

Page

CHAPTER 2 EXPERIMENTALS

CHAPTER 3 RESULTS AND DISCUSSION

CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

Hypochlorite is a very important disinfectant and is used as a powerful oxidizing agent. It plays a very important role in the field of paper and pulp industries,jute,cotton and leather industries as bleaching agent. It is used for sterilization of water in both drinking and swimming pools. It is a very useful oxidizing agent for converting Cr^{3+} to chromate, Pb salt to PbO_2, arsenites to arsenates etc. Hypochlorite is not only a stronger oxidizing agent than chlorine but is much more reactive and can bleach more rapidly at room temperature. Alongwith othar industries,Paper and pulp,cotton and leather industries are considered as the major industries in Bangladesh. To develop a method for the production of hypochlorite which is a very essential chemical substance used in the above mentioned industries is of worth investigation.

Hypochlorite has drawn our attention because of its wide application and can be produced from sodium chloride which is easily available in Bangladesh.

Hypochlorite ion is formed by the donation of a pair of electrons by chloride ion to oxygen atom.

$$\overset{-}{\underset{\times\times}{\overset{\times\times}{{}^{\times}_{\times}Cl^{\times}_{\times}}}}\ \underset{\circ\circ}{\overset{\circ\circ}{O}}{}^{\circ}_{\circ} \longrightarrow (\overset{-}{Cl}\rightarrow O) \longrightarrow ClO^{-}$$

The hypochlorite can be produced by using different methods,e.g. sodium hypochlorite is obtained in solution by passing chlorine into a cold, dilute solution of sodium hydroxide or sodium carbonate.

$$2NaOH + Cl_2 = NaCl + NaOCl + H_2O$$

$$Na_2CO_3 + Cl_2 = NaCl + NaOCl + CO_2$$

A solution of hypochlorite is produced by electrolysing a cold solution of sodium chloride. The mixing of the chlorine and caustic soda first formed and then react to form hypochlorite.

In Bangladesh, Chittagong Chemical Complex produces chlorine and sodium hydroxide by the electrolysis of sodium chloride but proper attention is not paid to the production of hypochlorite. The plant only produces a mixture of a solution of sodium and calcium hypochlorite by passing directly chlorine to the solution of calcium and sodium hydroxide, a limited amount of it is supplied in the market as hypochlorite. No mention is made about the concentration of hypochlorite. These are mainly used in big hotels of Bangladesh and are not available in local market.

A good number of researchers have studied on the electrolysis of sodium chloride solution but not much attention have been paid to the hypochlorite production by this method. The commercial use of electrochemical methods for producing hypochlorite and chlorate from chloride probably antidated by a few years, the first successful commercial electrochemical production of alkali and chlorine.

In these early cells, the production efficiency was low and production was only economical where electrical energy was quite cheap,inasmuch as the simple addition of chromate to prevent cathodic reduction of hypochlorite and chlorate had not yet been discovered.

Originally,platinum was used as an anode material,cells being operated at high temperatures and high anode current densities to maintain maximum current afficiencies with a minimum investment in platinum. Modern cells employ graphite or in a few cases magnetite anode. With platinum anode, the cell can be operated at high temperature. With graphite anodes,low cell temperatures are maintained to prevent anode dissolution. All installations in the United States now employ graphite anodes.

Among the published investigations on electrochemical production of hypochlorite and chlorate, the comprehensive work of F. Foerster[1] is of the paramount importance even after 35 to 40 years. The literature of the commercial processes have been published for Pennsylvania Salt Company by Anon[2] and the Western Electrochemical Company by Schumacher[3].

Studies on carbon or graphite anodes have been made by Sproesser[4], Linari and Pietra[5] and a series of papers published by the Burea of Agriculture[6,7]. Landolt et al[8] have investigated the mechanism of hypochlorite and chlorate formation in an electrolytic cell. The reactions that took place in the cell were according to Foorster[1] and Müeller[9] formulation. M.S. Ali[10] studies the same system using thin film bipolar rod cell.

In the present investigation, an attempt has been made on the production of hypochlorite by the electrolysis of sodium chloride using simpler electrolytic cell. Graphite has been used as anode and stainless steel as cathode. During electrolysis, chlorine was evolved at the anode and hydrogen at the cathode. Chlorine and hydroxyl(OH^-) produced in the cell reacted in the bulk to form hypochlorite. The amount of hypochlorite produced was determined iodometrically.

The objective of this project was to develop an electrochemical method for the optimum production of hypochlorite. The power consumption, current efficiency and space time yield were also studied.

1.2 BASIC PRINCIPLE FOR THE PRODUCTION OF HYPOCHLORITE

N.IBL and D. Landolt[8] have described the theory of electrolysis of sodium chloride in detail. Hypochlorite is manufactured industrially by the electrolysis of neutral sodium chloride solution. The main reactions taking place in a hypochlorite cell were formulated by Foerster[1] and Müeller[9]. The primary product of electrodes reactions, chlorine and alkali, react in the bulk of the electrolyte to form hypochlorite.

According to Foerster[1] and Mueller[9], the reactions taking place in the cell are as follows :

At the anode; $2Cl^- \longrightarrow Cl_2 + 2e$ . . . . (1.1)

At the cathode; $2H_2O + 2e \longrightarrow H_2 + 2OH^-$ . . .(1.2)

Solution ; $Cl_2 + H_2O \longrightarrow HOCl + Cl^- + H^+$..(1.3)

$HOCl \rightleftharpoons OCl^- + H^+$ . . . (1.4)

Chlorine forming at the anode and the hydroxyl ions forming at the cathode react with each other according to the following reactions.

In a neutral medium,

$Cl_2 + H_2O \longrightarrow HOCl + Cl^- + H^+$. . . . .(1.5)

In an alkaline medium,

$Cl_2 + OH^- \longrightarrow OCl^- + Cl^- + H^+$ . . . . (1.6)

1.3 LOSS OF CURRENT EFFICIENCY DUE TO SIDE REACTIONS AT THE ANODE.

In practice 100% current efficiency is not really possible since losses occur due to side reactions at the anode and cathode. At the anode, the most important undesirable electrode reaction is the oxidation of hypochlorite or its acid to chlorate. Instead of reacting chemically in the solution the hypochlorite ion diffuses back to the anode and is oxidised there. The reaction have been formulated by Foerster as :

$$6\ OCl^- + 3H_2O \longrightarrow 2\ ClO_3^- + 4Cl^- + 6H^+ + 3/2\ O_2 + 6e \ \ldots(1.7)$$

$$\text{or}\ \ 6\ HOCl + 3H_2O \longrightarrow 2ClO_3^- + 4Cl^- + 12H^+ + 3/2\ O_2 + 6e \ \ldots(1.8)$$

According to reaction(1.7) and(1.8) Foerster bases his equation on the hypothesis that hypochlorite is oxidised to chlorine monoxide.

$$6\ ClO^- \longrightarrow 6\ ClO + 6e \ \ldots\ldots\ldots\ldots \ (1.9)$$

The chlorine monoxide so formed on the electrode reacts with water to form chlorate and oxygen.

$$6\ ClO + 3H_2O \longrightarrow 2\ ClO_3^- + 4\ Cl^- + 6H^+ + 3/2\ O_2 \ \ldots(1.10)$$

Some times per-chlorate may be formed from chlorate,

$$ClO_3^- + H_2O \longrightarrow ClO_4^- + 2H^+ + 2e \ \ldots\ldots\ldots \ (1.11)$$

Reaction (1.11) occurs only at very high potential. For example,it occurs at magnetite anodes,which have a high over voltage and is negligible at graphite anodes.

Foerster stated that in a mildly alkaline solution a third reaction " The so called primary chlorate formation " occurs.

$$ClO^- + 2O \longrightarrow ClO_3^- \ \ldots\ldots\ldots\ldots \ (1.12).$$

This would represent a direct oxidation of hypochlorite by absorbed oxygen.

In industry it is impossible practically to suppress completely the anodic oxidation of hypochlorite to chlorate.

Smaller current efficiency is lost if some of the current is used to discharge hydroxyl ions :

$$OH^- \longrightarrow H^+ + \frac{1}{2} O_2 + 2e \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1.13)$$

Decomposition of hypochlorite in the electrolyte may be formed in the following way[11]

$$2HClO \longrightarrow 2HCl + O_2 \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1.14)$$

The consumption of hypochlorite due to chemical formation of chlorate according to the following reactions (1.15) and (1.16) can be suppressed either by electrolysis at a very low temperature ($0^\circ C$) or at high pH (> 9).

$$2HClO + OCl^- \longrightarrow ClO_3^- + 2Cl^- + 2H^+ . \; . \; . \; . \; . \; . \quad (1.15)$$

$$HClO + 2ClO^- \longrightarrow ClO_3^- + 2Cl^- + H^+ \; . \; . \; . \; . \; . \; . \; . \; . \quad (1.16)$$

1.4 LOSS OF CURRENT EFFICIENCY DUE TO THE SIDE REACTIONS AT THE CATHODE

The cathodic (or reduction efficiency) losses occur on the cathode surface and are due to

(1) Reduction of hypochlorite

$$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2OH^- \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1.17)$$

(2) Reduction of chlorate

$$ClO_3^- + 3H_2O + 6e^- \longrightarrow Cl^- + 6OH^- + \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1.18)$$

In accordance with the well known chemical properties of these ions,hypochlorite is much more easily reduced than chlorate.

The cathodic losses were studied by Nagai and Takei.[12] Their results indicated that these losses were governed by diffusion of hypochlorite towards the chthode surface.

Nagai. T and Takei. T[13] also found that during the electrolytic production of chlorate with chromium plated cathode,cathodic reaction took place at first but decreased after a certain time. This effect was due to the formation of a thin layer containing chromium at the cathode surface, which affected the rate of diffusion of hypochlorite.

If the hypochlorite ion diffuses to the cathode, it is reduced to chloride. This can be avoided by adding some dichromate to the electrolyte provided the latter is weakly acidic,neutral or alkaline. Dichromate is added to the electrolyte to suppress reduction of hypochlorite at the cathode. The action of the chromate is explained by the formation of a thin film of chromium oxide on the cathode surface which reduces the reduction of hypochlorite.

1.5 INFLUENCE OF IMPURITIES IN THE ELECTROLYTE

For the industrial production of hypochlorite sodium chloride are generally used. Sodium chloride may contain calcium or magnessium as impurities. The impurities such as calcium or magnessium (as low as 5 mg ca per litre) can deposit on the cathode. This can be minimized by the addition of complex forming reagent or by the addition of a "cleaning " cell working infront of the cell at a high current density. The best solution appears to be the occasional washing of the cell.

1.6 ELECTRODES MATERIALS

Good-ridge and King[14] suggested the following desirable properties for a prospective electrode materials for synthesis.

(a) It should be a good conductor.

(b) It should not suffer chemical or electrochemical attack.

(c) The surface should be an effective catalyst for the reaction in question when possible.

(d) It should usually be of rigid construction.

Since anodes often suffer from considerable corrosion problems,it is convenient to consider anode and cathode materials separately.

1.6.1 ANODE MATERIALS

Pink and Pan[15] enunciated six basic requirements that should be satisfied by anode materials for hypochlorite production.

(a) The anode materials should resist oxidation or attack by such substances as sodium chloride,hypochloric acid,hypochlorous acid,hypochlorite,chlorate,chlorine gas and oxygen.

(b) The anode materials must be a good conductor.

(c) The anode materials must not have a high initial cost.

(d) The anode materials should be mechanically storng.

(e) The anode materials should have a low electrode potential or low chlorine over-voltage.

(f) The anode materials even when going into solution due to corrosion must not contaminate or affect the cell product or products.

1.6.2 GRAPHITE ANODE

The commercial introduction of graphite anodo to the electrochemical field contributed in a large measure to the rapid and successful development of the alkali-chlorine industry.

Most of the basic requirements for anode materials are met by graphite[15].

The chemical attack of graphite anode may be considered due to the presence of available chlorine,hypochlorous acid, hypochlorite,chlorate and evolution of anodic oxygen during brine electrolysis. The available chlorine in the cell under steady condition is govarned by the current density,temperature,degree of conversion of hypochlorite to chlorate and also on the other factor such as concentration of chloride and electrolyte pH.

For a particular available chlorine content of the brine, as the current density and chloride concentration increases and temperature of the cell decreases, the concentration polarisation of the hypochlorite ion discharge will decrease aod graphite consumption will be reduced. The anode current losses are considered as a direct function of chemical attack and corresponding graphite wear.

The formation of chlorine dioxide during electrolysis of sodium chloride solution with graphite anode was observed by Western and Hooglan[16]. During electrolysis of sodium chloride with graphite anodes, hypochlorite, chlorate, chlorine and chlorine dioxide may be formed, the chemical oxidation of graphite with these compounds may proceed as follows :

$$C + 2\ HClO \longrightarrow CO_2 + 2H^+ + 2Cl^- \quad \ldots\ldots\ldots \quad (1.19)$$

$$C + ClO_2 \longrightarrow CO_2 + \tfrac{1}{2}\,Cl_2 \;.\;.\;.\;.\;.\;.\;.\;.\; (1.20)$$

$$3C + 2ClO_3^- \longrightarrow 3CO_2 + 2Cl^- \;.\;.\;.\;.\;.\;.\;.\;.\; (1.21)$$

$$3C + 2\,Cr_2O_7^{=} + 16H^+ \rightleftharpoons 3CO_2 + 4Cr^{3+} + 8H_2O \;.\;.\;.(1.22)$$

According to Eberil,Elina[17], these reactions are thermodynamically quite possible, chromate acting internally as well as externally to wear away the graphite electrode and for this reason its concentration should be minimised.

Bauer[18] suggested graphite anode covered with an electrochemically deposited lead dioxide layer, which would minimise anode attack. Sampath and others[19] investigated the electrolysis product of sodium chloride in 200 ampere cell using lead dioxide coated graphite anodes and stainless steel cathodes. The cell was run continuously with a view to evaluting the life of these anodes. It was found that the materials gives excollent service, remaining unaffected after 24 months of continuous running. In the case of hypochlorite production, the low cell tamperature is required,hence graphite anode is very important in this condition.

1.6.3 PLATINUM ANODES

Katzen and Sokolov[20] electrolysed sodium chloride solution using platinum anode and obtain current efficiency of(90-92)%. The problem is that the cells are operated at high temperature[21] where hypochlorites are oxidised to chlorate. For the maximum production of hypochlorite, low cell temperature is required and graphite anode is very effective. The use of platinum as an electrode material is economically not viable.

1.6.4 MAGNETITE ANODES

The magnetite anodes used in the commercial cells are made of hamatite, the inner surface being coated with a layer of electro deposited copper. Magnetite anodes have low conductivity. The electrical voltage of the cells and consequent consumption of energy are high. Cells provided with magnetite electrodes can be operated with a good current efficiency of about 83-86% only, and chlorate concentrations of maximum of 280-300 gm $NaClO_3$ per litre can be obtained. When higher concentration are used the current yields fall rapidly. In acid electrolytes, undesirable formation of per-chlorate take place. When magnetite electrodes are used, the heat developed is high. In order to maintain the cells at the favourable operating temperature of 70°C, large quantities of cooling water are required. The high temperature favours the formation of chlorate from hypochlorite. The disadvantages of low conductivity and tendency to perchlorate formation are avoided when graphites anodes are used in stead of megnetite anode.

In Japan, magnetite anodes were used in a chlorate plant in 1934 at Shivakawa because of the limited availability of graphite,63% of the annual chlorate production of the plant described is derived from magnetite anode cell.

T. Matsumura[22] employed the laboratory date to optimise the cell operating conditions of the commercial cell. Optimum pH was 6.75,current efficiency increased with increasing temperature. An improvement in ventilating conditions was also effective. As a result, a current efficiency of 83-85% and electric power consumption of 5900-6300 kWh/Ton of $NaClO_3$ were obtained. Magnetite anode cells permit high temperature operation that accelerate the chemical chlorate formation. The magnatite anodes are no longer in use because of high over voltage.

1.6.5 GRAPHITE SUBSTRATE LEAD DIOXIDE ANODE

Bauer[18] suggested graphite anodes electrochemically deposited with lead dioxide layer in which anode attack would be minimised,if lead dioxide electrodes could be substituted for platinum in the production of perchlorates. The preparation of electrodes suitable for use in commercial cells have been developed by Udupa et al[23]. The electrodes have the following advantages over the electrodes developed in Japan by Sugino and Shibasaki[24] and Suginok[25].

(i) A thin coating of lead dioxide on graphite or carbon is adequate for the use of electrode.

(ii) The graphite or carbon is completely protected against anodic attack.

(iii) Electrical contact can be made conveniently on lead dioxide surface.

(iv) Preparation of such electrodes for large scale operation does not present undue difficulty.

The use of lead dioxide anode is not restricted to the production of perchlorate alone[26],it can be successfully used for the preparation of chlorate also. A comparison of the performance of a lead dioxide coated graphite anode and that of a conventional graphite anode under identical conditions of operation in a chlorate cell was made by Udupa et al[27]. Udupa et al did an experiment for the preparation of sodium hypochlorite and chlorate employing 200 amp. cell with lead dioxide coated anode and stainless steel cathode. The cell was run continuously to evaluate the life of the anodes.

Lead dioxide coated graphite anodes have the advantage of a longer life over the conventional graphite anodes and can conveniently replace the graphite anodes,leading to substantial savings in initial as well as recurring costs. A current efficiency of 75-80 percent can be obtained by using lead dioxide anodes. Problems with lead dioxide coating on graphite anodes appeared to be made with adhesive and homogeneous lead dioxide layers. Until now cylindrical anode have been produced which are not useful for large scale.

1.6.6 TITANIUM ANODE

Titanium is malleable and ductile metal resembling iron compounds are fairly widely distributed in nature, but the metal is difficult to extract. Titanium anodes activated with other metals have yielded interesting results, both with respect of electrode life as well as energy usage. Titanium anodes had been activated with platinum-Iridium in the ratio of 70:30 could at 60°C, with an anodic current density 3300 Am^{-2} and an average cell voltage of 3.5V was run for 27 months before the activation decreased the effectiveness in a krebs type 6 kilo ampere chlorate cell. At that point 20% of the original pt-Ir layer was still present. Fleck[28] showed that deactivation effect occured using Titanium anodes activated with Ruthenium dioxide after 12 months.

1.7 CATHODES

Cathodic losses have been studied by Nagai and Takei[12] The main problem in finding a suitable cathode material lies in the minimisation of reduction losses of hypochlorite. Steel cathodes are effectively protected from corrosion at current density larger than 300 Am^{-2}. This is important since iron ions catalytically decompose hypochlorite and chlorate ions.

Nagai, T and Takei, T[13] also found that during electrolytic production with a chromium plated cathode, cathodic reduction took place at first but decreased after certain time. This was due to the formation of a thin layer containing chromium at the cathode surface,which affected the rate of diffusion of hypochlorite. By using a cathode of chromium or chromium plated stainless steel,cathodic reduction of hypochlorite ion can be efficiently suppressed without adding dichromate. The action of chromium plated cathodes in proventing reduction seems to be due to the chromium being superficially oxidised by hypochlorites and then to a lower oxide[29]. This explantion is in accordance with Liebreich[30] and Wielder Holt[31]. Presumably the action of this chromium oxide layer is similiar to that produced from dichromate in the electrolyte. It appears that a chromium-plated electrode develops an active surface and a matt chromium surface is more active than a bright one for reduction. A metal such as chromium and Molybdenum on the cathode surface of graphite electrodes decrease the required cell voltage and power consumption as found by Jaksic et al[32].

1.8 CURRENT EFFICIENCY

The current efficiency of hypochlorite may be defined as the ratio of tha actual amount of hypochlorite produced to that expected theoretically based on the quantity of current passed.

Current efficiency (C.E) of hypochlorite

$$= \frac{\text{Actual amount of hypochlorite produced}}{\text{Theoretical amount of hypochlorite to be produced}} \times 100$$

based on the quantity of current passed.

$$= \frac{W}{Z.\ I.\ t} \times 100 \quad \dots\dots\dots\dots\dots\dots \quad (1.23)$$

$$= \frac{W.F}{I.\ t.\ e} \times 100 \quad \dots\dots\dots\dots\dots\dots \quad (1.24) \left\{ Z = \frac{e}{F} \right.$$

Where, W = Actual amount of hypochlorite produced in gms.

F = Faraday's constant.

Z = Electrochemical equivalent of hypochlorite.

I = Actual current passed in amp.

e = Equivalent weight of hypochlorite.

t = The time required for electrolysis in second.

1.9 SPACE TIME YIELD

The space time yield of hypochlorite may be defined as the amount of hypochlorite produced per hour per cubic meter of the cell.

Space time yield (Y_{st}).

$$= \frac{\text{Amount of hypochlorite produced}}{\text{(Time of electrolysis) x (volume of the cell).}} \ \text{kgh}^{-1}\ \text{m}^{-3}$$

1.10 POWER CONSUMPTION

The amount of hypochlorite produced in kg or in ton per kilowatt-hour (kWhr) is called the power consumption of hypochlorite.

$$\text{Power consumption} = \frac{\text{kWhr.}}{\text{kg of hypochlorite}}$$

$$= \frac{\text{Voltage} \times \text{Ampere} \times \text{Time (min)}}{1000 \times \frac{g}{1000} \times 60}\ \text{kWhr/kg}$$

$$= \frac{V.A.t\ (\text{min})}{g \times 60}\ \text{kWhr/kg.}$$

$$= \frac{V.A.t\ (\text{min}) \times 1000}{g \times 60}\ \text{kWhr/Ton}$$

Where, V = Voltage

A = Ampere

t = Time in minute

g = Production of hypochlorite in gm. during electrolysis.

CHAPTER 2

EXPERIMENTALS

EXPERIMENTALS

2.1 INTRODUCTION

A number of experiments were performed in a novel cell for the production of hypochlorite and also chlorate as secondary product. A new cell system was developed for this purpose to get a cell of simple geometric shape, ease of design and can be easily constructed. Graphite anodes and stainless steel cathodes have been used which are cheap and easily available material.

In the present investigation, it was aimed to study the optimum production of hypochlorite, power consumption and space time yield. To obtain larger amount of hypochlorite (amount of chlorate was kept at minimum) different variables have been studied for this purpose. The variablee studies were current density, temperature, pH, concentration, cell number and with or without the addition of dichromate to the electrolyte.

Most of the experiments were carried out with 4.0 M NaCl solution. Current density was varied between 187.5 to 750 Am^{-2} and pH between 6 to 10 at room temperature.

Low temperature favours the hypochlorite formation but due to the non-available cooling system in the laboratory, the experiments were carried out at room temperature. Some experiments were performed by adding dichromate to the electrolyte to suppress the reduction of hypochlorite at the cathode.

2.2 CELL DESIGN

The process of alkali chloride electrolysis is very sensitive to cell design that has been recognised from its early stages and various types of cells are available[33,34,35,36]. However, the nature of the cell depend on the end product required. In hypochlorite production, it is recommended that the electrolytic equipment should not be made of metal as the latter would take part in the reduction of the hypochlorite causing efficiency losses. Dimensionally stable anodes such as Pt, Ti/TiO_2 are preferable but high cost prevents its use. In the present study graphite has been chosen as anode because at low temperature of operation it does not errode. The outer frame of the cell body should be made of inert material such as pyrox glass and perspex. In the design of the new cell these factor have been taken into consideration. The description of the cell is given in the next section.

2.3 DESCRIPTION OF THE CELL

The design of the cell for the present investigation was developed to obtain maximum current efficiencies and optimum production of hypochlorite by the electrolysis of sodium chloride. The cell system consisted of perspex box in which anode and cathode were placed. Two boxes of different sizes were used to study the effect of amount of electrolyte on the hypochlorite production. The boxes measuring (33 cm x 23 cm x 19 cm) and (26 cm x 8 cm x 14 cm) were used.

The electrolytic cells consisted of graphite anodes and stainless steel cathodes which were rectangular in shape and placed virtically in the perspex box. The number of the cells in the perspex box were 8 (eight). In each cell a graphite anode and a stainless steel cathode were placed vertically at a distance of 10 mm and one cell was kept apart from another by a distance of 15 mm. The graphite anoda measuring (5 cm x 4 cm x 0.635 cm) and cathode measuring (5 cm x 4 cm x 0.317 cm) were used. The stainless steel wire was used to keep the electrode in position.

The anodes of all the cells were connected in series by a conducting wire to the positive pole and all the cathodes to the negative pole of the power supply via an ammeter and a voltmeter in the circuit as shown in figure 2.2 and 2.3. The complete view of the experimental setup is shown in figure 2.4. Figure 2.1 shows the dimension of anode and cathode.

The experimental box for electrolysis consisted of two stop cocks D_1 and D_2 of which D_1 was the inlet through which electrolyte was introduced in to the experimental box and D_2 outlet was used to collect the electrolytic sample for analysis.

2.4 INSTRUMENTATION AND MATERIALS

INSTRUMENTATION

(1) A manually controlled power supply having an out put 0-15 Amperes and 0-30 volts.

(2) An ammeter ranging from 0-15 Amperes and a voltmeter ranging 0-30 volts.

(3) A pH meter,
Corning Medical and Scientific, Halsteed, Essex CO92DX, England.

(4) Graphite anode and stainless steel cathode.

(5) Two experimental perspex boxes of different size in which electrolysis were performed.

(6) A stop watch.

(7) Aspirator bottles(10 lit, 5 lit, and 2½ litres capacity).

MATERIALS

(1) Hydrochloric acid(conc.) . . . .(BDH)

(2) Sulphuric acid(conc.) . . . .(BDH)

(3) Potassium dichromate . . . .(E.Merck).

(4) Sodium chloride . . . .(E.Merck).

(5) Sodium chloride . . . .(Local).

(6) Potassium Iodide . . . . (E.Merck).

(7) Sodium bicarbonate . . . . (E.Merck).

(8) Sodium thiosulphate . . . .(E.Merck).

(9) Silver nitrate . . . . (E.Merck).
(10) Starch indicator . . . . (E.Merck).
(11) Potassium chromate . . . . (E.Merck).
(12) Double distilled water

2.5 PROCEDURE

The experimental box was fitted with electrodes and were connected to the power supply having an ammeter and a voltmeter in the circuit. In most of the experiments 4.0 M sodium chloride (234 gm/lit) solution were used and in some of the experiments potassium dichromate (2.5 gm/lit) had been added to increase the hypochlorite production. The temperature and pH of the electrolyte were recorded for every experiment. The electrolytic products were collected through the outlet at an interval of 10 or 20 minutes for analysis.

The main products in the electrolysis of sodium chloride were hypochlorite and chlorate, these were analysed by iodometric titration.

CALCULATION OF THE AMOUNT OF HYPOCHLORITE PRODUCED

The amount of hypochlorite produced during electrolysis were determined by iodometric titration[10]. A sample of usually 20 ml was taken in a conical flask from the electrolytic solution. 1 ml of 1N sodium bicarbonate was added and mixed by gentle shaking. After the addition of 5 ml 10% potassium iodide and 5 ml of 1M sulphuric acid, the flask was covered with a watch glass,shaked and allowed to stand for 3-5 minutes in darkness. It was then titrated against 0.1N sodium thiosulphate using starch indicator. The volume V_1 of sodium thio-sulphate required for titration was noted at the end point and was used to calculate the amount of hypochlorite.

CALCULATION OF THE AMOUNT OF CHLORATE PRODUCED

The amount of chlorate produced during electrolysis was determined by iodometric titration. 20 ml of the electrolytic solution was taken in a conical flask, 5 ml of 10% potassium iodide,20 ml of distilled water and 50 ml of concentrated hydrochloric acid were added to it. The flask was covered with a watch glass,shaked and allowed to stand for about 5 minutes in darkness. The liberated iodine was then titrated against 0.1N sodium thiosulphate solution using starch solution as indicator. The volume V_2 of sodium thiosulphate was noted at the and point. Now the difference between V_2 and V_1 was the actual volume of sodium thiosulphate required for the titration and was used to determin the amount of chlorate.

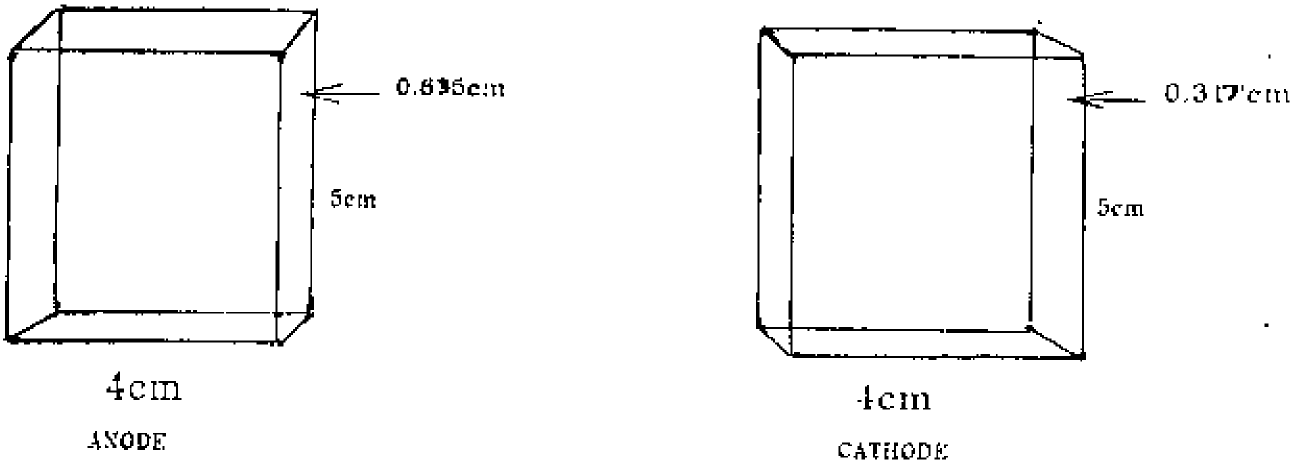


FIGURE 2.1 ELECTRODE USED IN THE ELECTROLYTIC CELL

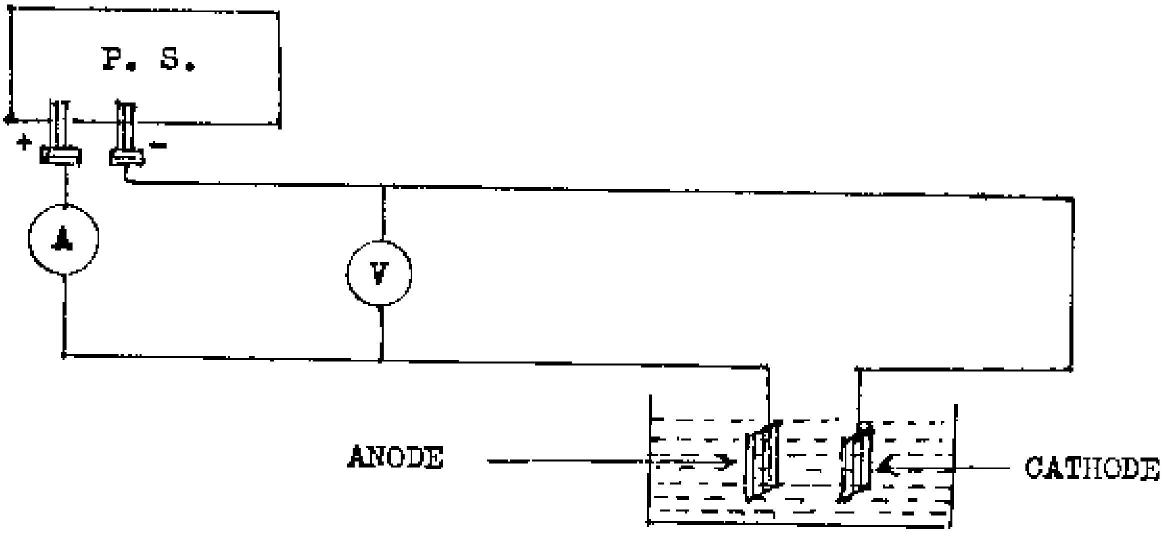


FIG: 2.2 A SET-UP FOR A SINGLE ELECTROLYTIC CELL

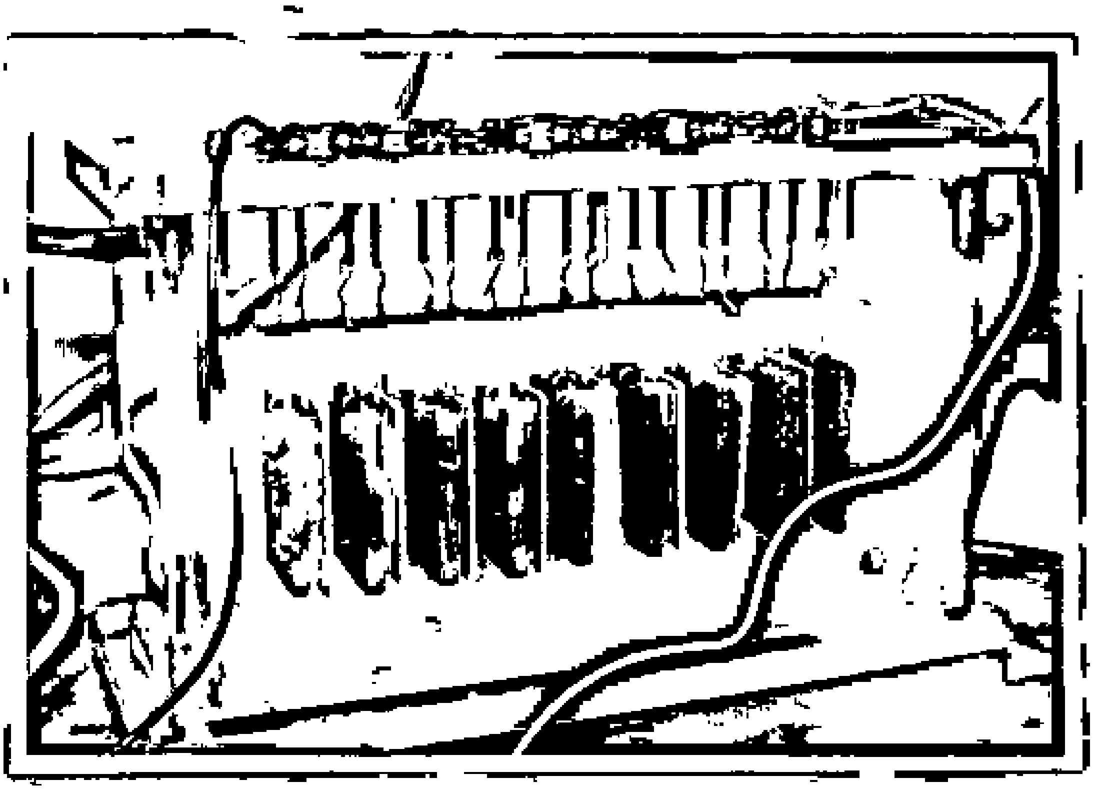


FIGURE 2.3 : SET-UP OF ELECTRODES IN THE BOX.

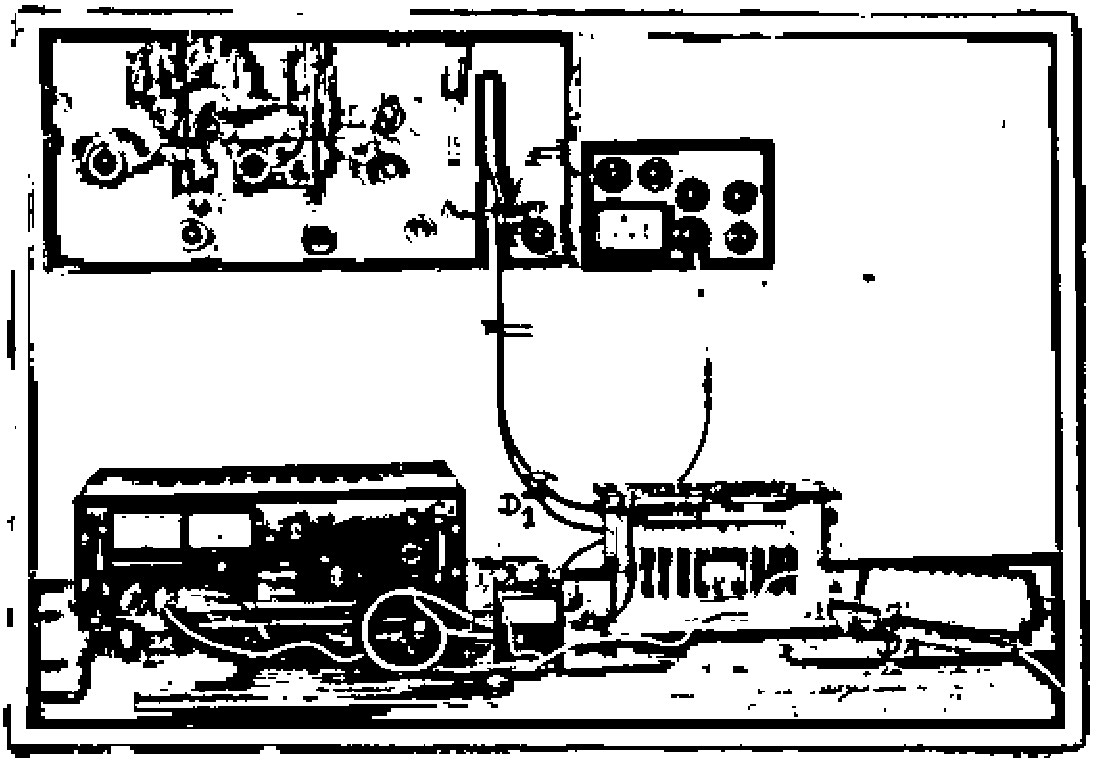


FIGURE 2.4 : EXPERIMENTAL SET-UP.

CHAPTER 3

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

3.1 INTRODUCTION

An electrochemical cell system has been devised using graphite anode and stainless steel cathode for the production of hypochlorite by the electrolysis of sodium chloride solution. The performance of the cell for hypochlorite production has been assessed in terms of current efficiency,power consumption and space time yield.

The electrolysis of aqueous sodium chloride solution was started with 4.0M solution. Precautions were taken so that any unreacted chlorine produced during electrolysis could not escape. The amount of hypochlorite produced was determined at a suitable interval.

Experimental data and calculated results have been presented in Appendix and a selected number of experimental and calculated results are shown in this chapter. In each experiment the change of hypochlorite concentration with time was determined. The current efficiancy and space time yield for both hypochlorite and chlorate were also determined. The power consumption was calculated only for hypochlorite.

3.2 EFFECT OF TIME ON CONCENTRATION,CURRENT EFFICIENCY,SPACE TIME YIELD AND POWER CONSUMPTION OF HYPOCHLORITE :

Hypochlorite was produced at different operating current densities. A set of results at an operating current density of

375 Am^{-2} are shown in table 3.1 and have been plotted in figures 3.1,3.2,3.3 and 3.4.

Figure 3.1 represents the variation of concentration of hypochlorite and chlorate with time. It is observed from table 3.1 and figure 3.1 that the production of hypochlorite increases with increase of time upto certain period and then it decreases but the production of chlorate increases with time.

The variation of current efficiency of hypochlorite and chlorate production with time are shown in figure 3.2 which indicates that the current efficiency of hypochlorite remains almost constant up to certain period (about 100 minutes) and then it decreases but in the case of chlorate the current efficiency increases with time.

Figure 3.3 represents the variation of space time yield with time. It shows that the space time yield of hypochlorite decreasee with time but space time yield of chlorate goes on increasing. The variation of power consumption of hypochlorite with time has been plotted in figure 3.4 which shows that the power consumption increases with increase in time.

TABLE 3.1 PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D.375 Am^{-2}.

(1) Total current = 6 amp.
(2) Voltage = 6 volts.
(3) Total solution in the cell = 7 litres.
(4) Initial temperature = 23°C
(5) pH = 7.10

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ soln. ('0865N) required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	20	1.95	0.20	8.43	0.86	79.15	8.12	28.58	1.58
40	20	3.90	0.45	16.87	1.94	79.15	9.14	28.50	1.77
60	20	5.90	0.70	25.52	3.02	79.77	9.47	28.75	1.84
80	20	7.75	1.00	33.52	4.32	78.64	10.14	28.31	1.97
100	20	9.65	1.40	41.74	6.05	78.34	11.36	28.21	2.21
120	20	11.50	1.95	49.75	8.43	77.80	13.19	28.01	2.56
140	20	12.85	2.65	55.59	11.46	74.51	15.36	26.83	2.99
160	20	14.25	3.30	61.64	14.27	72.30	16.74	26.04	3.25
180	20	15.60	4.20	67.48	18.17	70.36	18.94	25.34	3.68
200	20	16.55	5.20	71.59	22.50	67.18	21.10	24.19	4.10
220	20	17.15	6.25	74.19	27.04	63.28	23.06	22.78	4.48
240	20	17.20	7.45	74.41	32.23	58.18	25.20	20.95	4.90
260	20	17.05	9.05	73.76	38.94	53.26	28.10	19.17	5.47

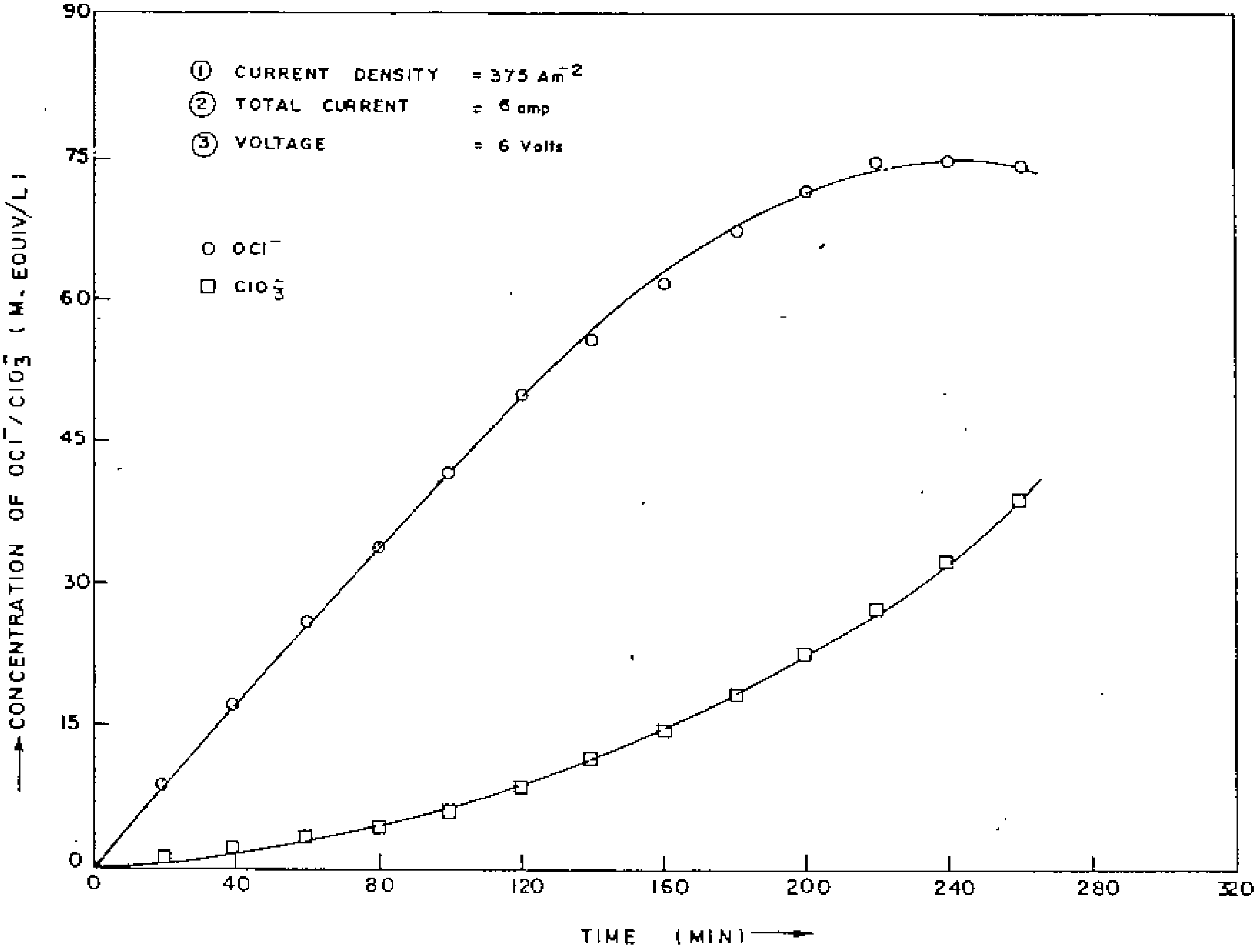


FIG. 3.1 VARIATION OF CONCENTRATION OF HYPOCHLORITE / CHLORATE WITH TIME.

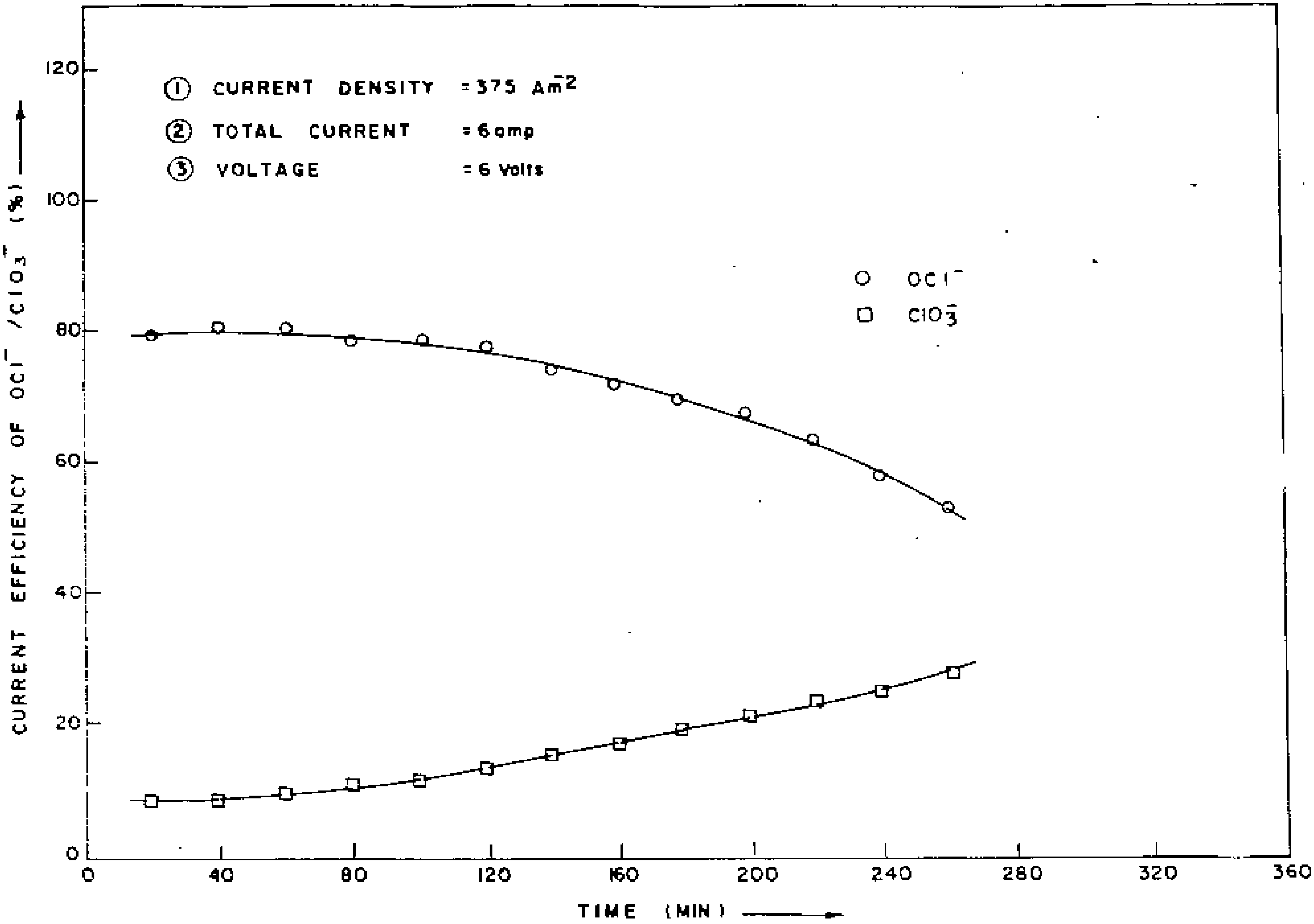


FIG. 3.2 VARIATION OF CURRENT EFFICIENCY WITH TIME

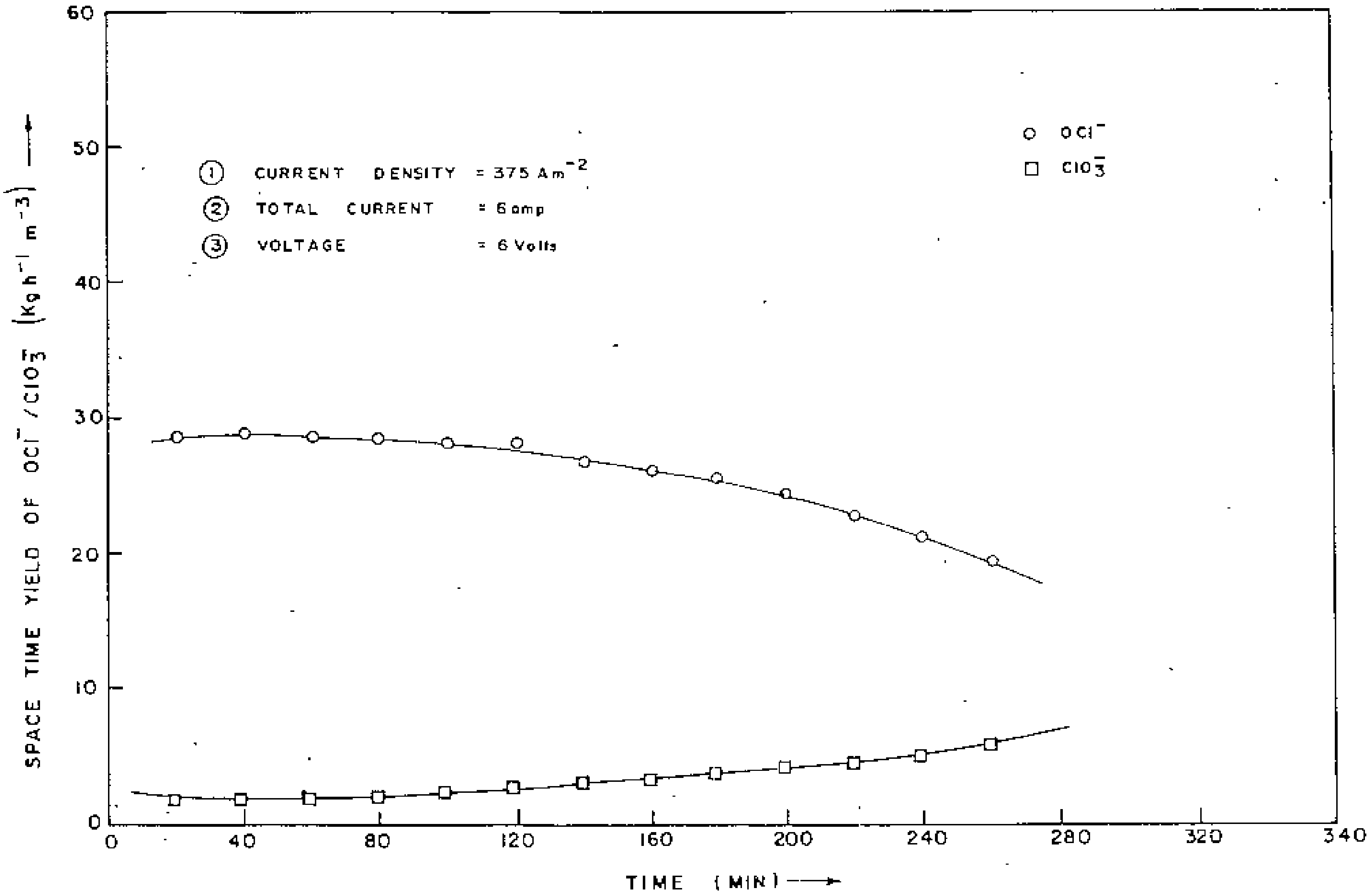


FIG. 3.3 VARIATION OF SPACE TIME YIELD ($kgh^{-1}\,m^{-3}$) WITH TIME.

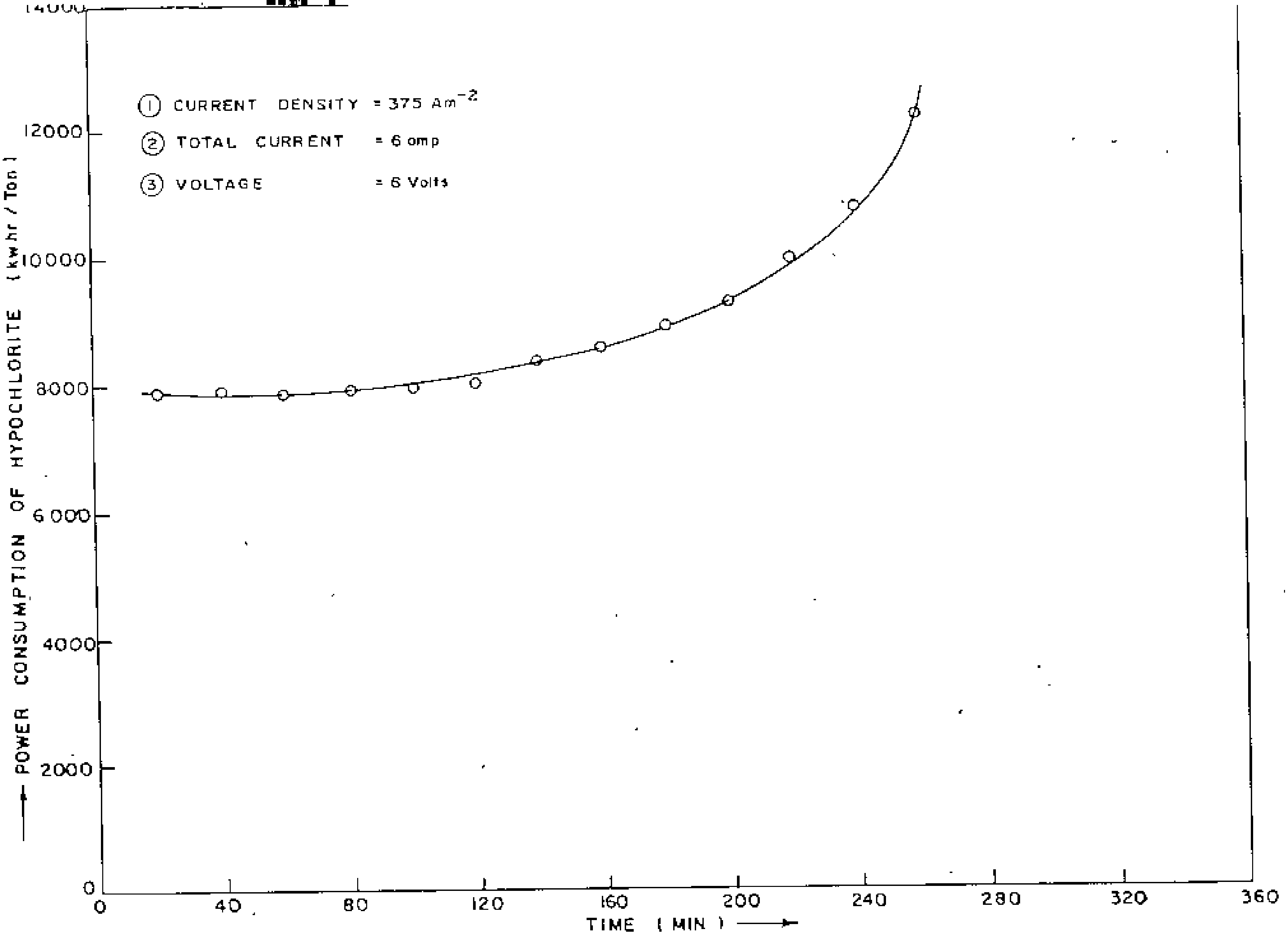


FIG. 3.4 VARIATION OF POWER CONSUMPTION OF HYPOCHLORITE WITH TIME

The decrease of current efficiency of hypochlorite production may be due to the oxidation of hypochlorite to chlorate,evolution of oxygen at the anode and reduction of hypochlorite at the cathode and chemical conversion of hypochlorite to chlorate. The amount of chlorate production increases with increase in time. This may be explained in the following way :

The hypochlorite ions (or its acid) formed in the solution diffuse back to the anoda and is oxidised there according to following reactions.

$$6\ OCl^- + 3H_2O \longrightarrow 2ClO_3^- + 4Cl^- + 6\ H^+ + 3/2\ O_2 + 6e.$$

or

$$6\ HClO + 3H_2O \longrightarrow 2ClO_3^- + 4Cl^- + 12H^+ + 3/2O_2 + 6e.$$

Chlorine monoxide may also be formed by the oxidation of hypochlorite

$$6\ ClO^- \longrightarrow 6ClO + 6e.$$

The chlorine monoxide so formed on the electrode reacts with water forming chlorate and oxygen.

$$6ClO + 3H_2O \longrightarrow 2ClO_3^- + 4Cl^- + 6H^+ + 3/2\ O_2.$$

Hammer and Wranglen[11] suggested that hypochlorite would be decomposed in the following way :

$$2\ HClO \longrightarrow 2\ HCl + O_2.$$

The consumption of hypochlorite may also occur according to the following reactions :

$$2\ HClO + ClO^- \longrightarrow ClO_3^- + 2Cl^- + 2\ H^+.$$

$$HClO + 2\ ClO^- \longrightarrow ClO_3^- + 2\ Cl^- + H^+.$$

Loss of current efficiency may occur due to the reduction of hypochlorite at the cathode surface in the following manner :

$$ClO^- + H_2O + 2e^- \longrightarrow Cl^- + 2\ OH^-.$$

The cathodic losses were studied by Nagai and Takei[12], their result indicate that these losses are governed by diffusion of hypochlorite towards the cathodic surface.

The results for operating current density of 625 Am^{-2} are shown in table 3.2 and in figures 3.5,3.6, 3.7 and 3.8. The results obtained in this case follow the same trend as observed in the previous case (C.D. 375 Am^{-2}). In every case,the experiments were repeated under the same conditions to obtain reproducible results.

A number of experiments were performed varying the current density from 187.5 Am^{-2} to 750 Am^{-2} in two perspex boxes of different sizes at different condition.

TABLE 3.2 PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 625 Am^{-2}.

(1) Total current = 10 amp.
(2) Voltage = 7 volts.
(3) Total solution in the cell = 8.30 litres.
(4) pH = 7.15
(5) Initial temperature = 22.5°C

Time of electrolysis (min)	Volume of electrolytic soln. analysed	Volume of $Na_2S_2O_3$ soln. (0.0913N) required for		Concentration (m.equiv /L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	20	2.45	0.25	11.80	1.14	74.62	7.61	44.81	2.46
40	20	4.90	0.55	22.36	2.51	74.65	8.38	44.81	2.71
60	20	7.30	1.00	33.32	4.56	74.13	10.15	44.50	3.29
80	20	9.60	1.40	43.82	6.39	73.12	10.66	43.90	3.46
100	20	11.85	1.80	54.09	8.21	72.21	10.97	43.35	3.55
120	20	13.60	2.20	62.08	10.04	69.06	11.17	41.46	3.62
140	20	15.30	2.75	69.84	12.55	66.59	11.97	39.78	3.88
160	20	16.55	3.40	75.55	15.52	63.03	12.95	37.84	4.20
180	20	18.05	4.15	82.39	18.94	61.11	14.05	36.68	4.55
200	20	19.05	4.95	86.96	22.59	58.04	15.08	34.84	4.89
220	20	19.45	5.80	88.78	26.47	53.87	16.06	32.34	5.21
240	20	19.50	7.00	89.01	31.95	49.51	17.71	29.72	5.76
260	20	19.20	8.70	87.64	39.71	44.99	20.38	27.01	6.60

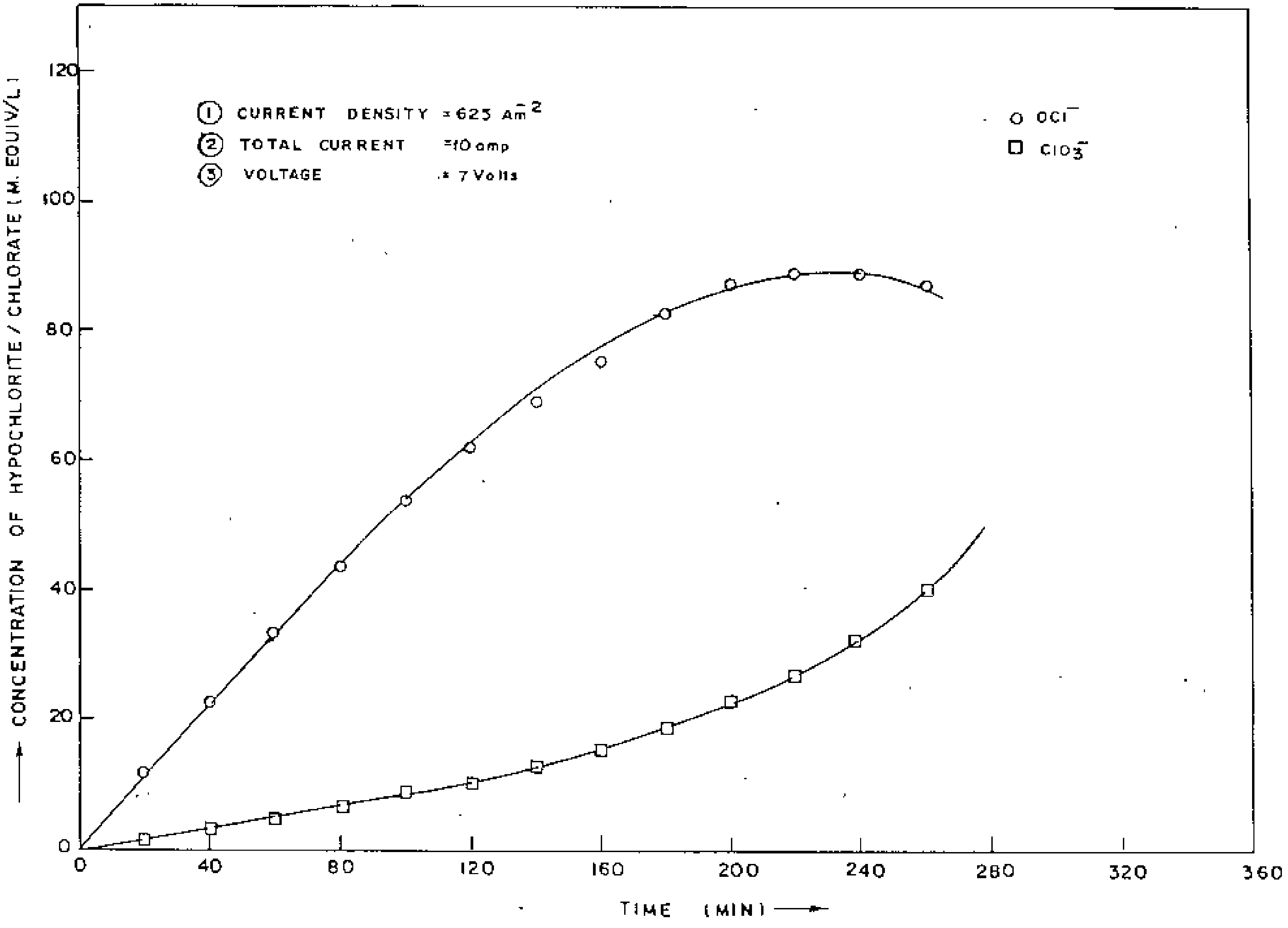
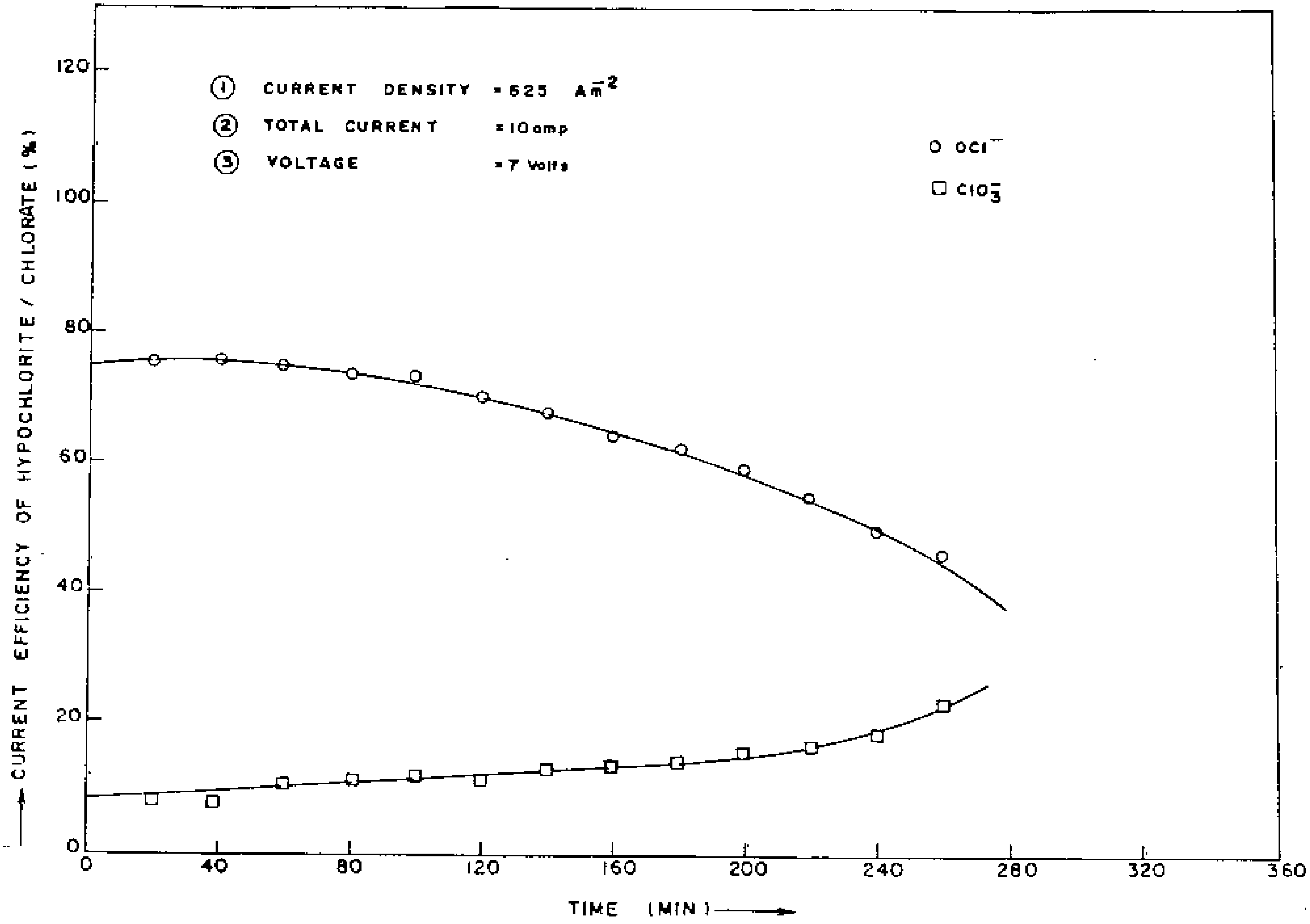


FIG. 3.5 VARIATION OF CONCENTRATION OF HYPOCHLORITE / CHLORATE WITH TIME.



FIG, 3.6 VARIATION OF CURRENT EFFICIENCY WITH TIME.

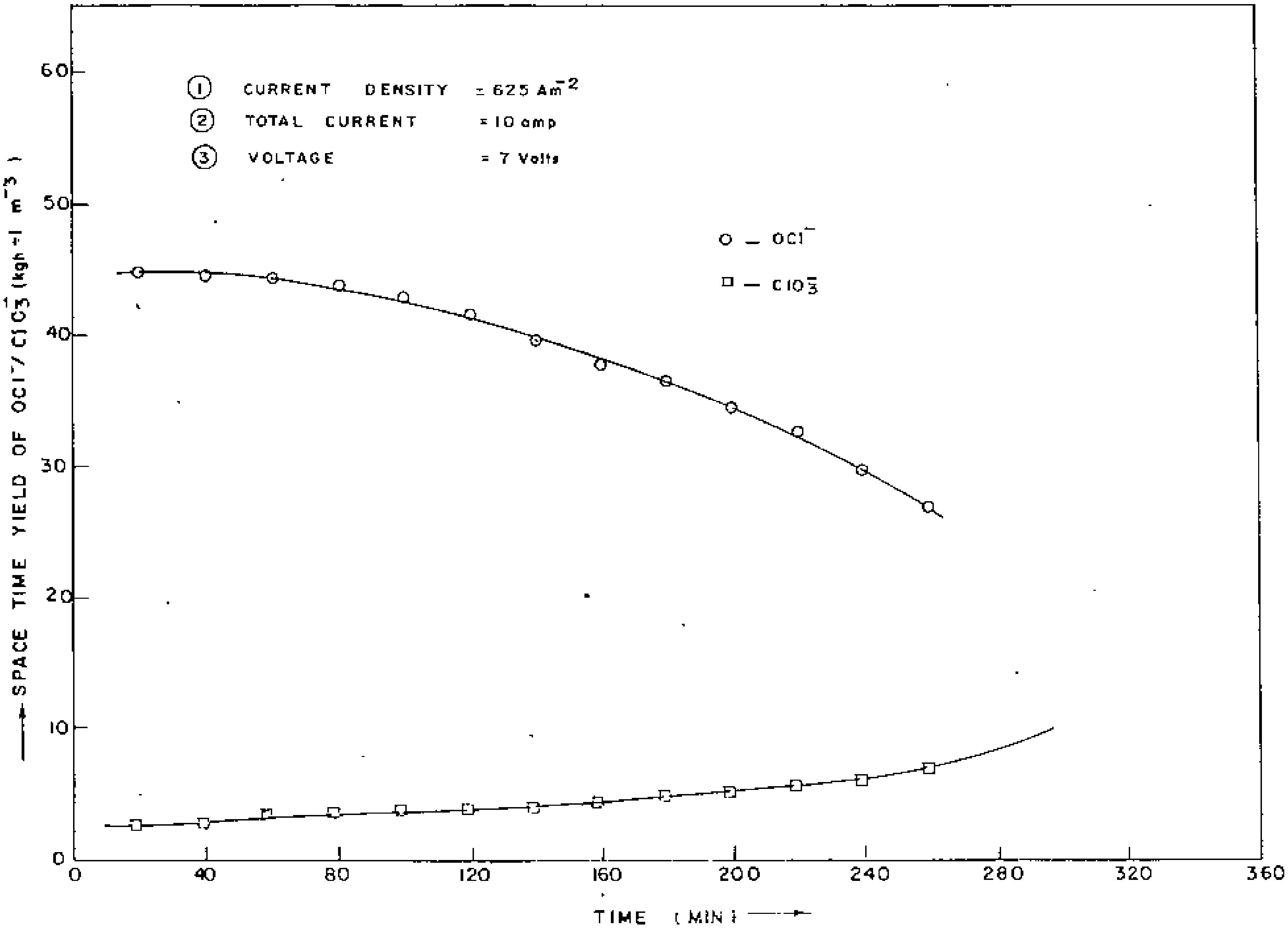


FIG. 3.7 VARIATION OF SPACE TIME YIELD WITH TIME.

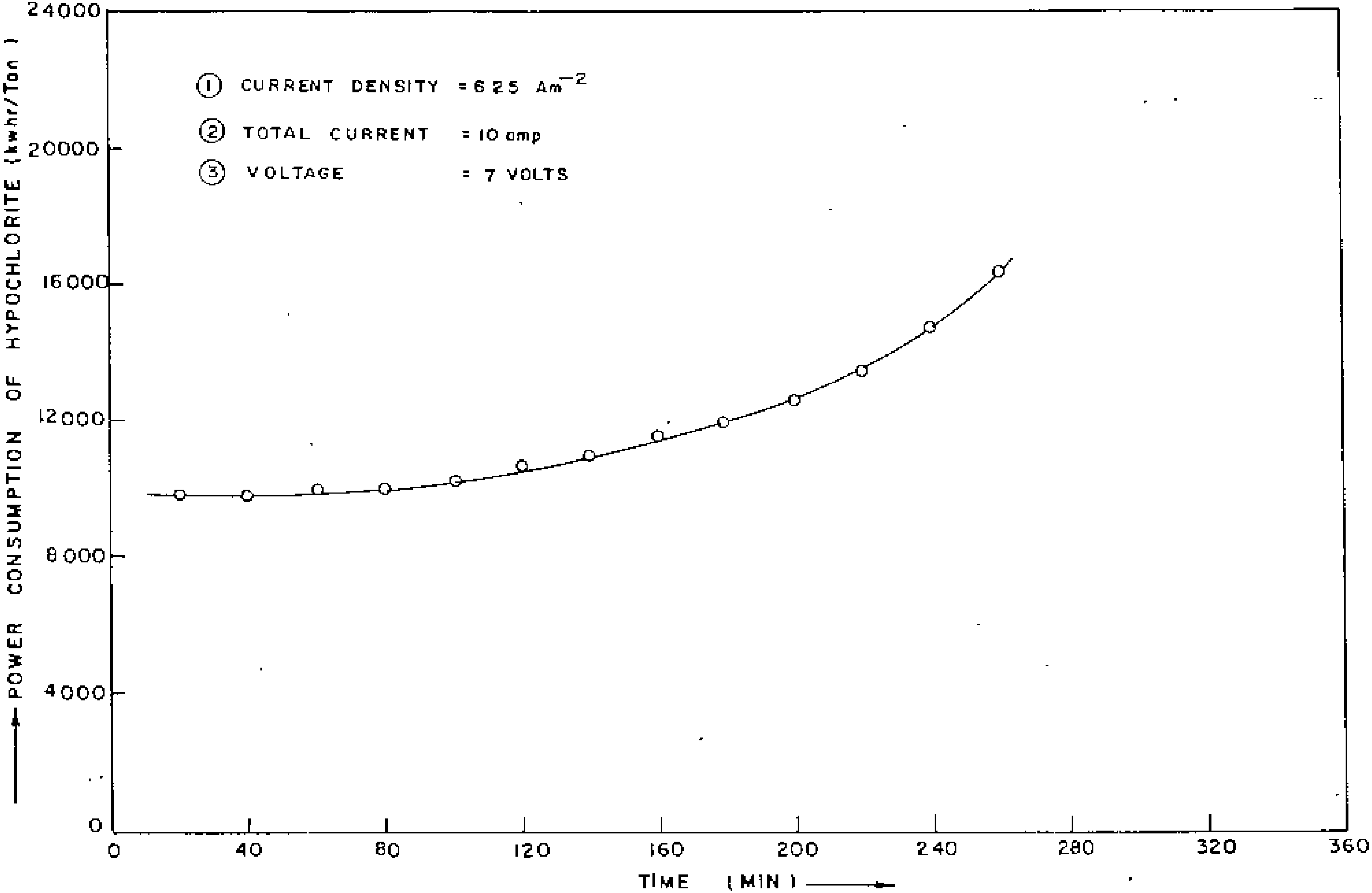


FIG. 3.8 VARIATION OF POWER CONSUMPTION OF HYPOCHLORITE (KWhr/Ton) WITH TIME.

The production of hypochlorite were found to be affected by the following variables :

(a) The effect of dichromate addition.
(b) The effect of current density.
(c) The effect of electrolytic temperature.
(d) The effect of pH value.

3.3 THE EFFECT OF DICHROMATE ADDITION

Experiments were run at the same current density with and without the addition of dichromate. The results have been discussed in terms of concentration, power consumption ,current efficiency and space time yield which are shown in figure 3.9,3.10,3.11 and 3.12 respectively.

It has been observed from the figures that the amount of hypochlorite production,current efficiency and space time yield increase due to addition of dichromate. However,power consumption is also less in this case for hypochlorite production.

During electrolysis there is a chance of reduction of hypochlorite to chloride which was usually avoided by the addition of dichromate. Dichromate forms a layer on the cathode surface and minimizes the diffusion of hypochlorite for reduction on the cathode,hence increases the amount of hypochlorite production.

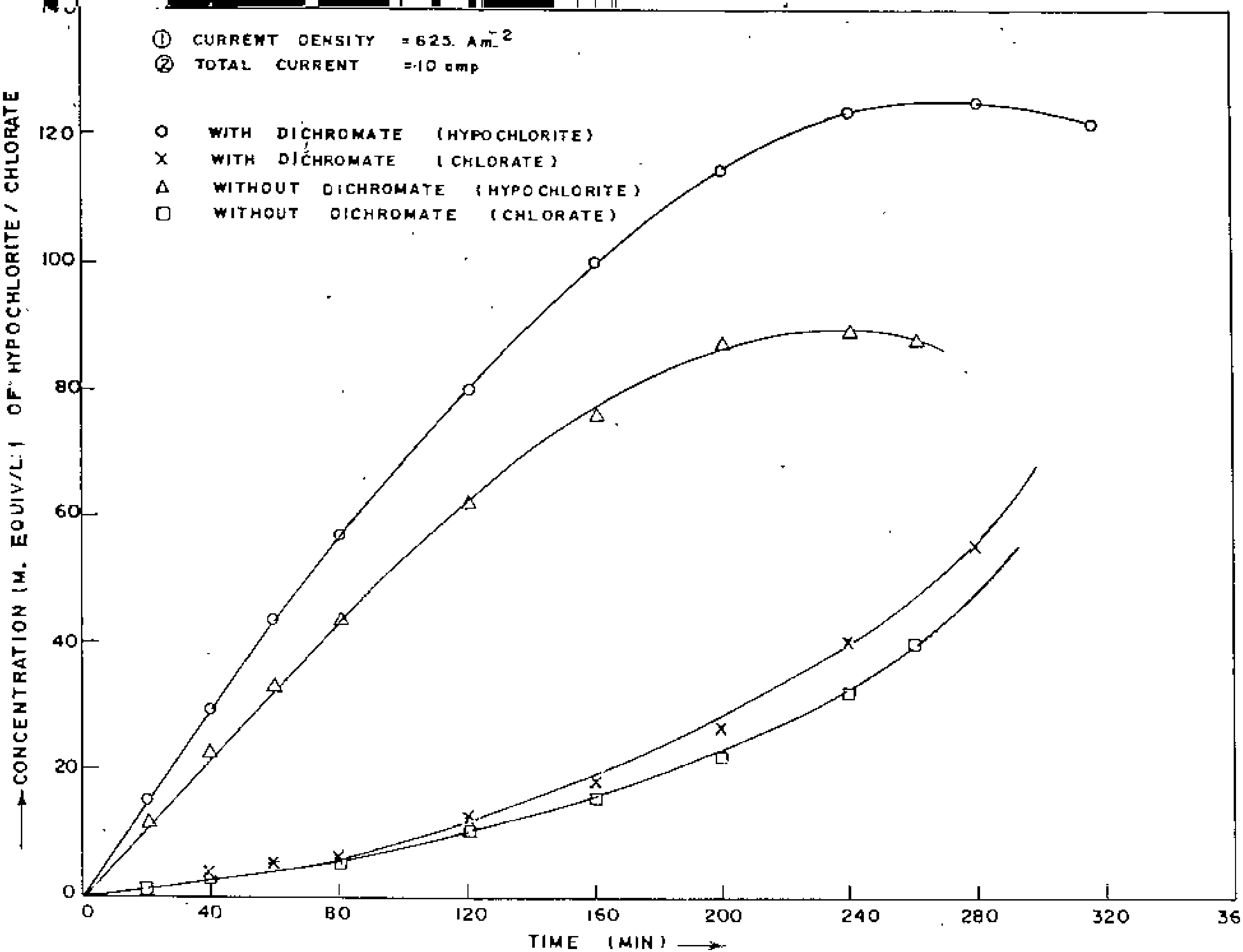


FIG. 3.9 VARIATION OF CONCENTRATION OF HYPOCHLORITE / CHLORATE WITH TIME USING DICHROMATE

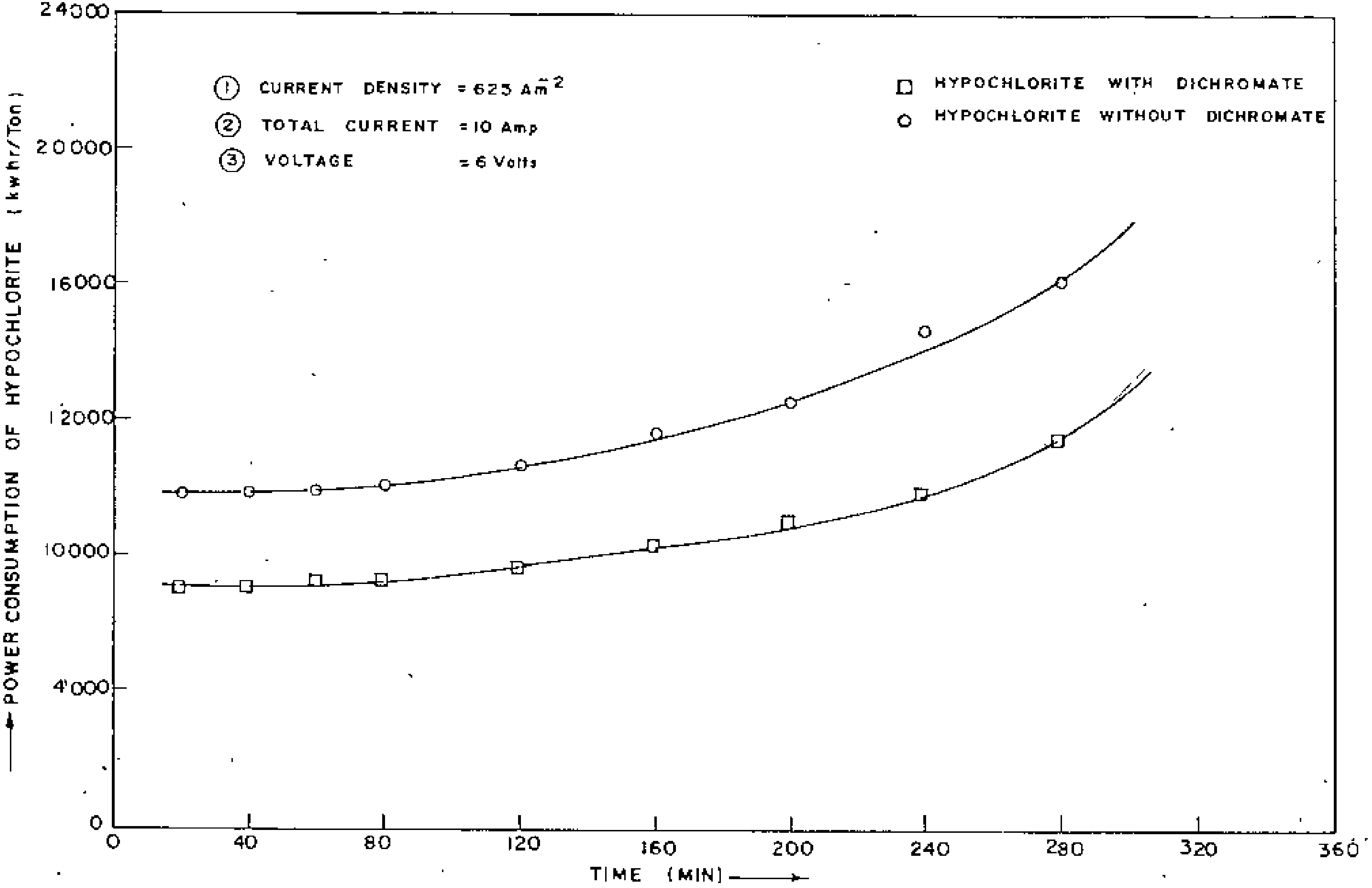


FIG. 3.10 VARIATION OF POWER CONSUMPTION WITH TIME USING DICHROMATE.

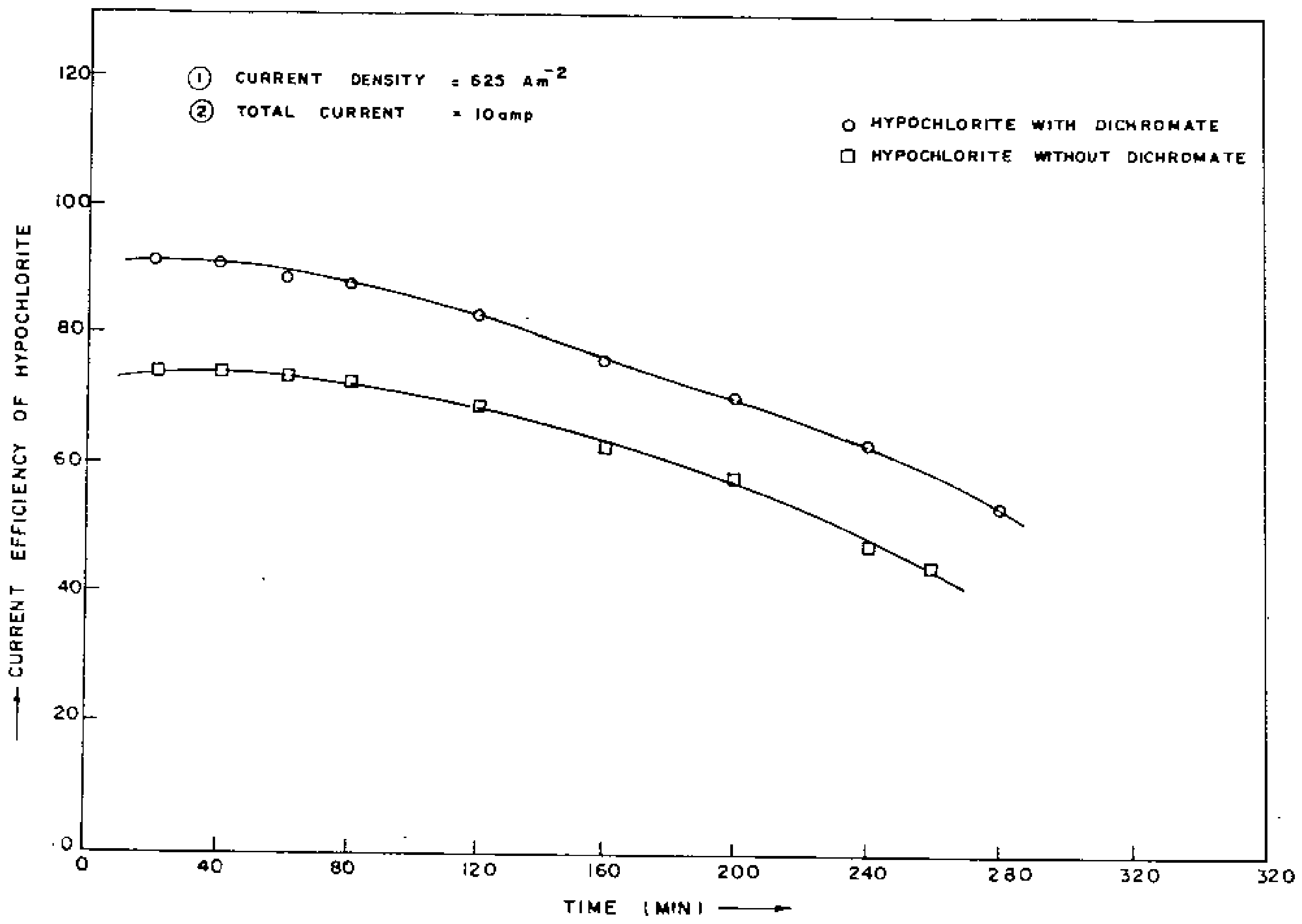


FIG. 3.11 VARIATION OF CURRENT EFFICIENCY WITH TIME WITH & WITHOUT DICHROMATE.

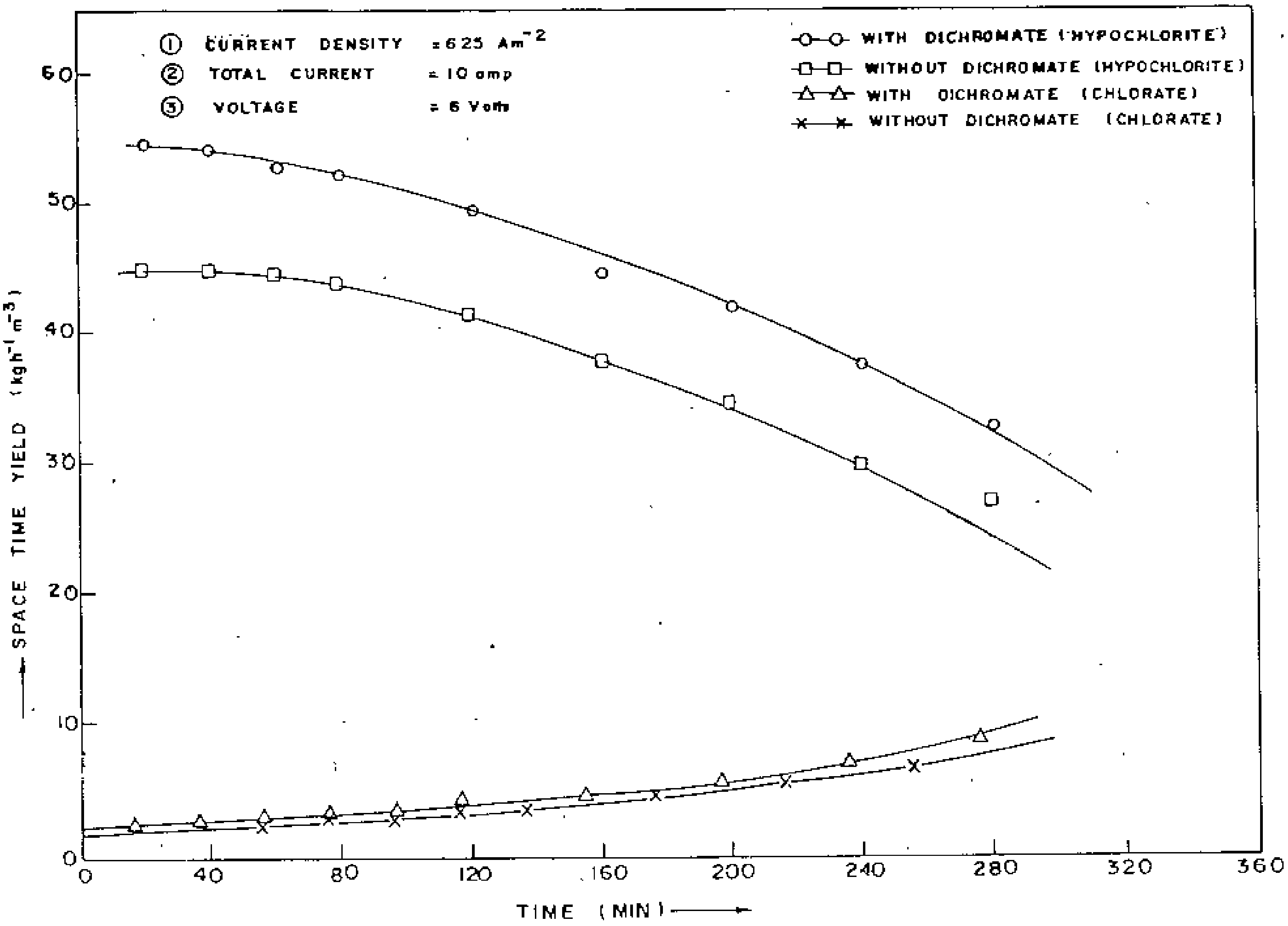


FIG. 3.12 VARIATION OF SPACE TIME YIELD OF OCl^-/ClO_3^- WITH TIME.

3.4 THE EFFECT OF CURRENT DENSITY

In figures 3.13,3.14 and 3.15 current efficiency,(maximum) power consumption (minimum) and space time yield (maximum) were plotted against current density respectively.

It can be observed that the current efficiency decreases with the increase of current density. At high current density the current efficiency decreasee although the hypochlorite production increases. Since the current efficiency decreases,the power consumption is also increased. The production of hypochlorite goes on increasing with the increase of current density. So the space time yield is also increased.

The loss of current efficiency may be attributed to the fact that at high current density the rate of electrochemical oxidation of hypochlorite to chlorate increases. The loss of efficiency may also be due to the escape of some amount of chlorine gases which are produced in large amount at high current density without being utilized for hypochlorite production. But at low current density the produced chlorine gases are mostly utilized for the production of hypochlorite.

3.5 THE EFFECT OF TEMPERATURE

In an electrochemical cell lower temperature is desirable for the production of hypochlorite. This has been varified in figures 3.17. It has been observed that at 22°C the amount of production and current efficiency of hypochlorite are greater than that at 33°C. But in the case of chlorate the production increases with increase in temperature.

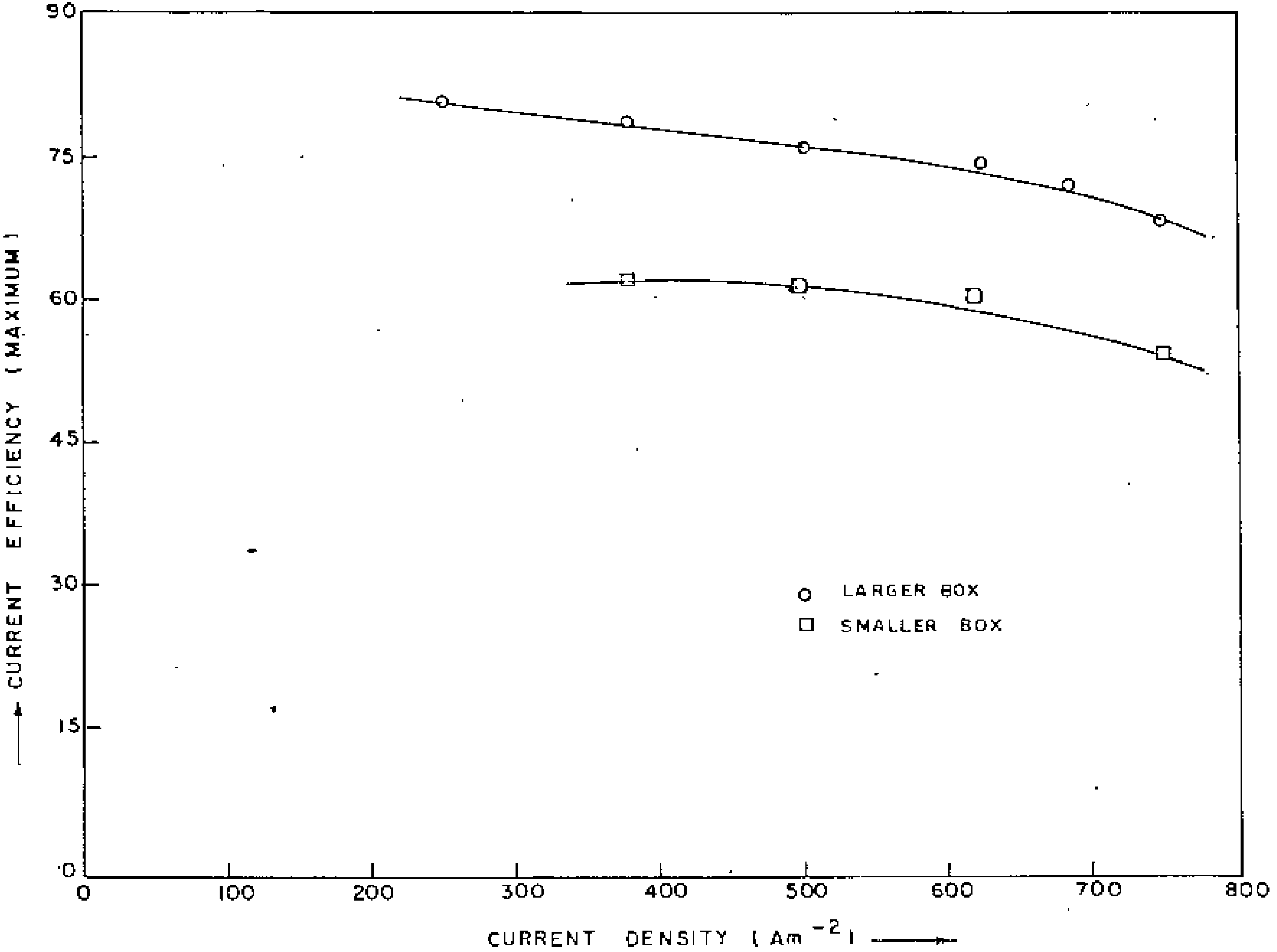


FIG. 3.13 VARIATION OF CURRENT EFFICIENCY WITH CURRENT DENSITY

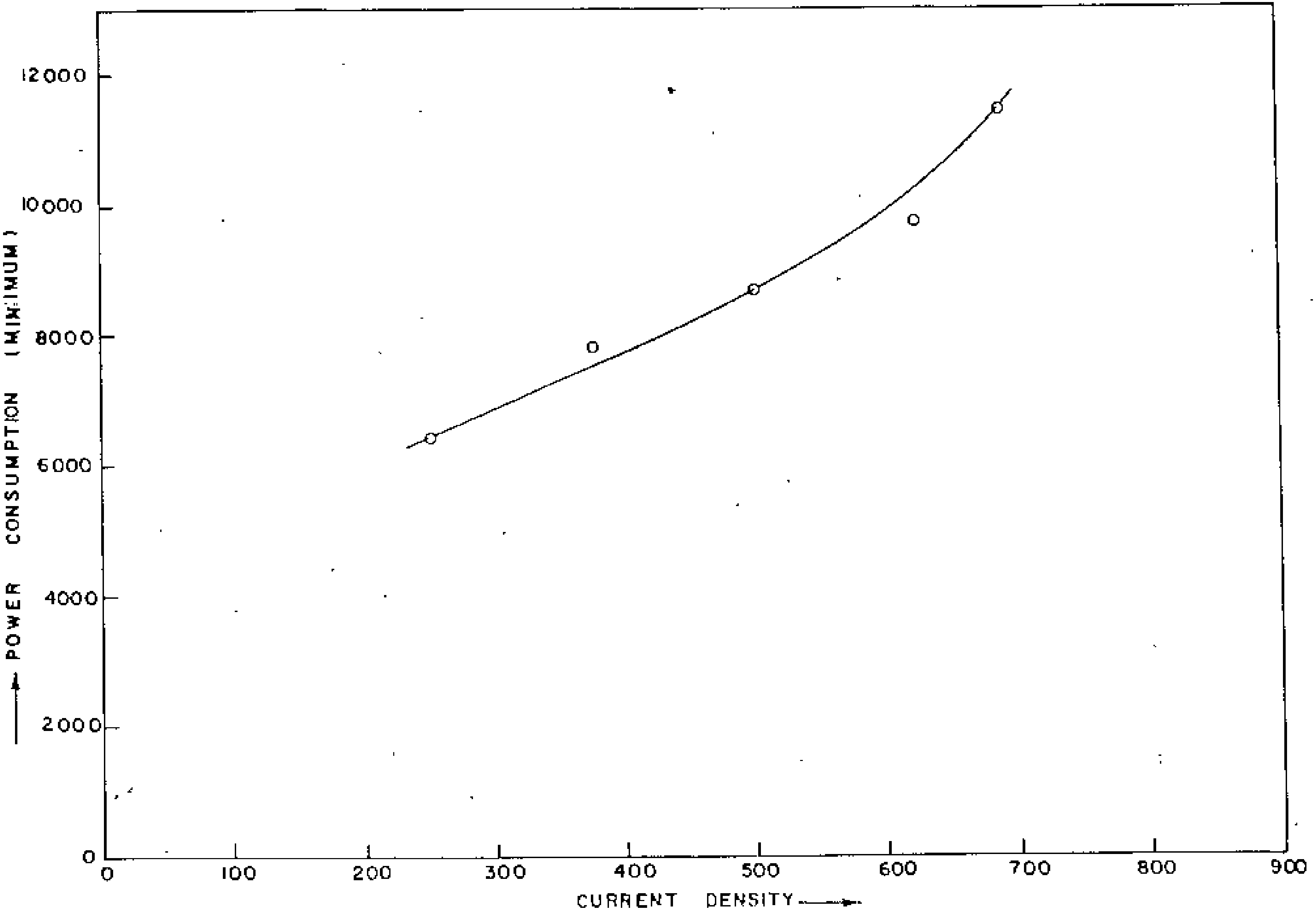


FIG. 3.14 VARIATION OF POWER CONSUMPTION WITH CURRENT DENSITY

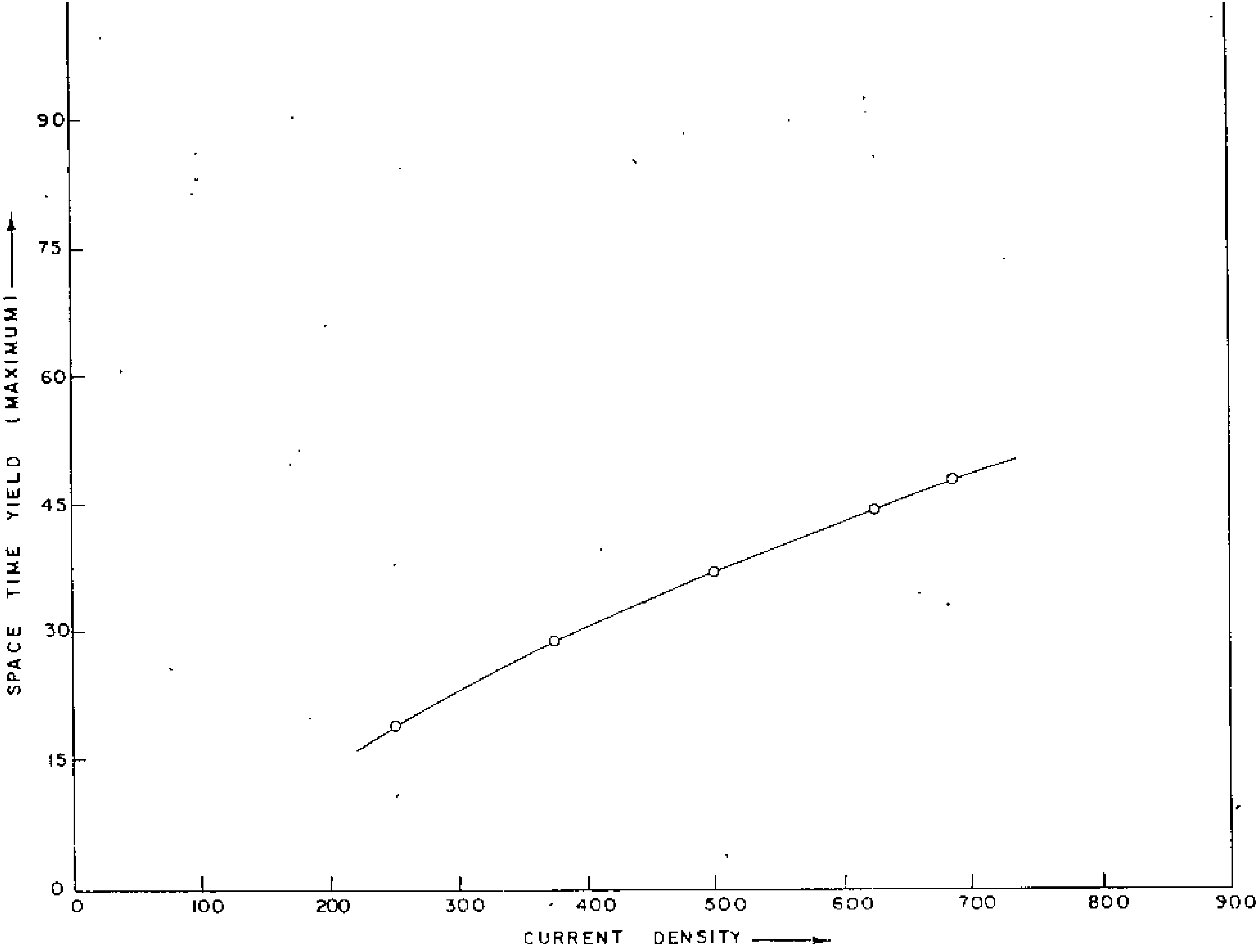


FIG. 3.15 VARIATION OF SPACE TIME YIELD WITH CURRENT DENSITY

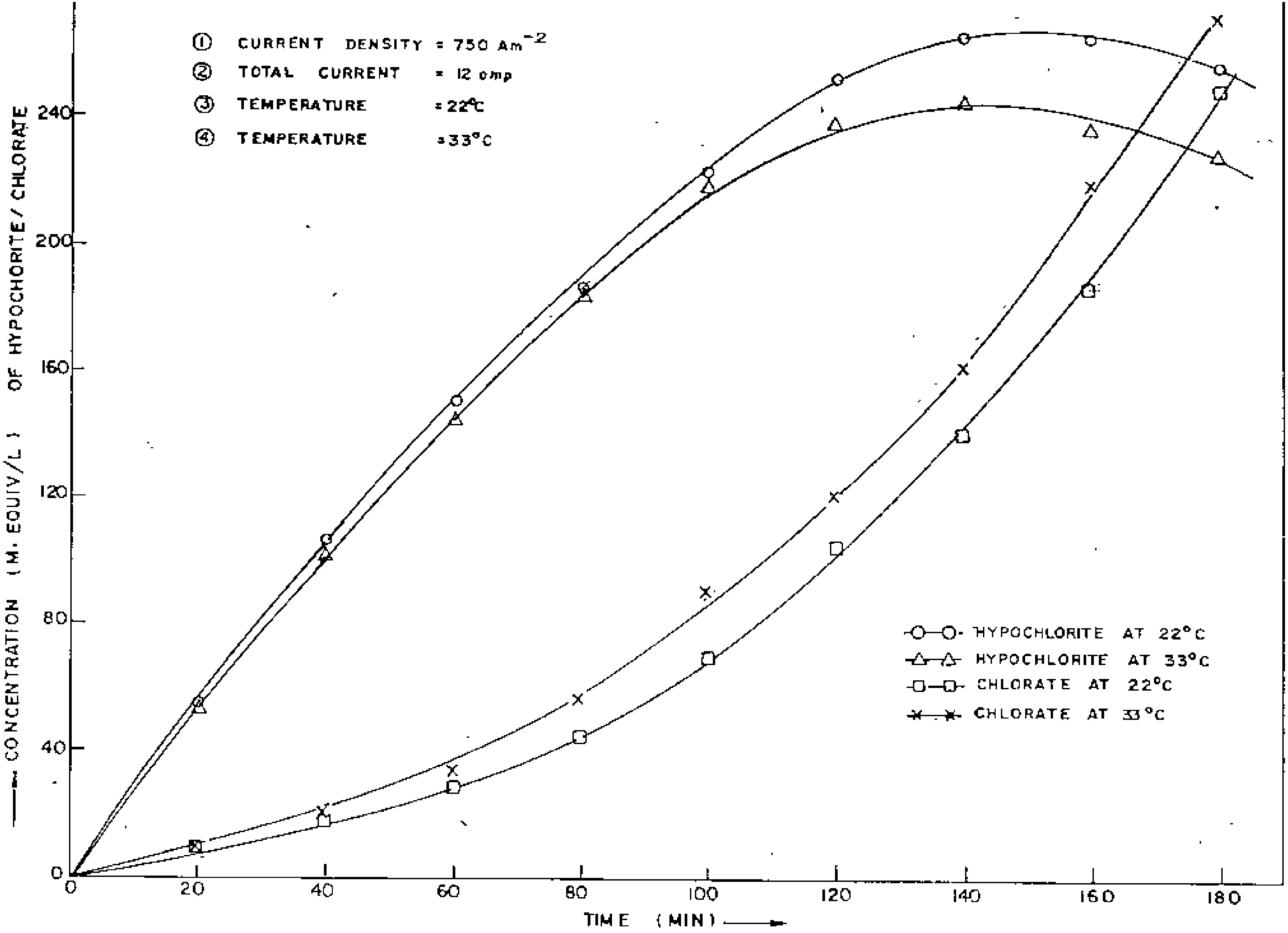


FIG. 3.16 VARIATION OF CONCENTRATION WITH TEMPERATURE

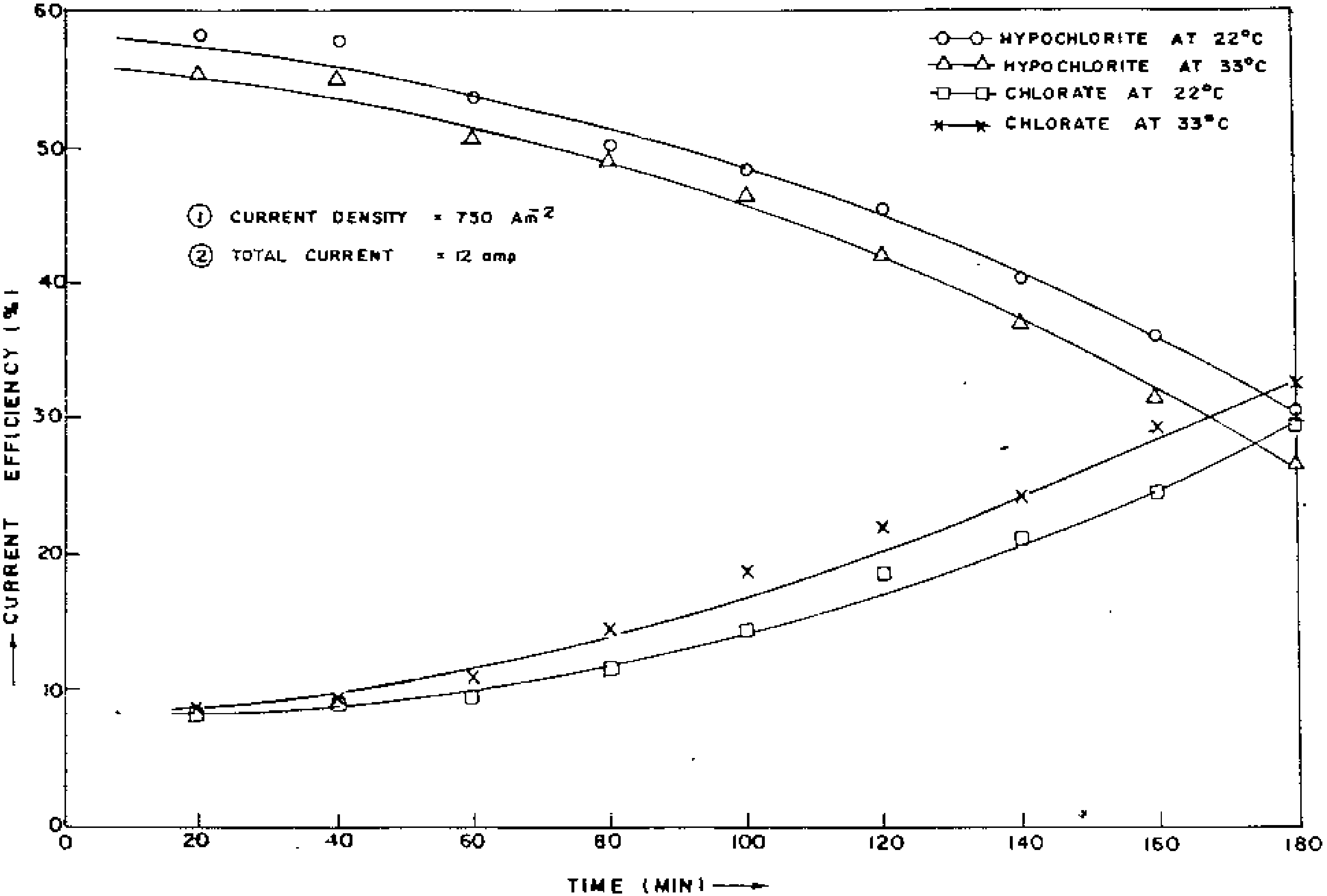


FIG. 3.17 VARIATION OF CURRENT EFFICIENCY WITH TIME

3.6 THE INFLUENCE OF pH

According to Hammer and Wranglen[11], the consumption of hypochlorite due to chemical formation of chlorate may be suppressed either by electrolysis at a very low temperature (0°C) or at high pH (>9). So most of the experiments were carried out at high pH to obtain the maximum production of hypochlorite.

3.7 THE EFFECT OF THE SIZE OF THE EXPERIMENTAL BOX

Two boxes of different sizes were used to construct the electrolytic cell having capacities of 10 litres and 2.5 litres. The current efficiency,production of hypochlorite and chlorate were found to be different for two boxes. Power consumption against current density and current efficiency against time for different current densities were plotted in figure 3.18 and 3.19. Power consumption for hypochlorite production was found to be higher in the case of smaller box but higher current efficiency was obtained for larger box at the same current density.

3.8 PERCENTAGE OF SODIUM CHLORIDE CONVERTED

Percentage of sodium chloride converted into hypochlorite and chlorate was plotted against time(figure 3.20). Initially the conversion of NaCl is rapid and then slows down. It attains a maximum of 15% at temperature 22°C and pH 9.15. A maximum conversion of 13% have been reported by Chittagong Chemical Complex,Bangladesh with 70°C at pH 6.5.

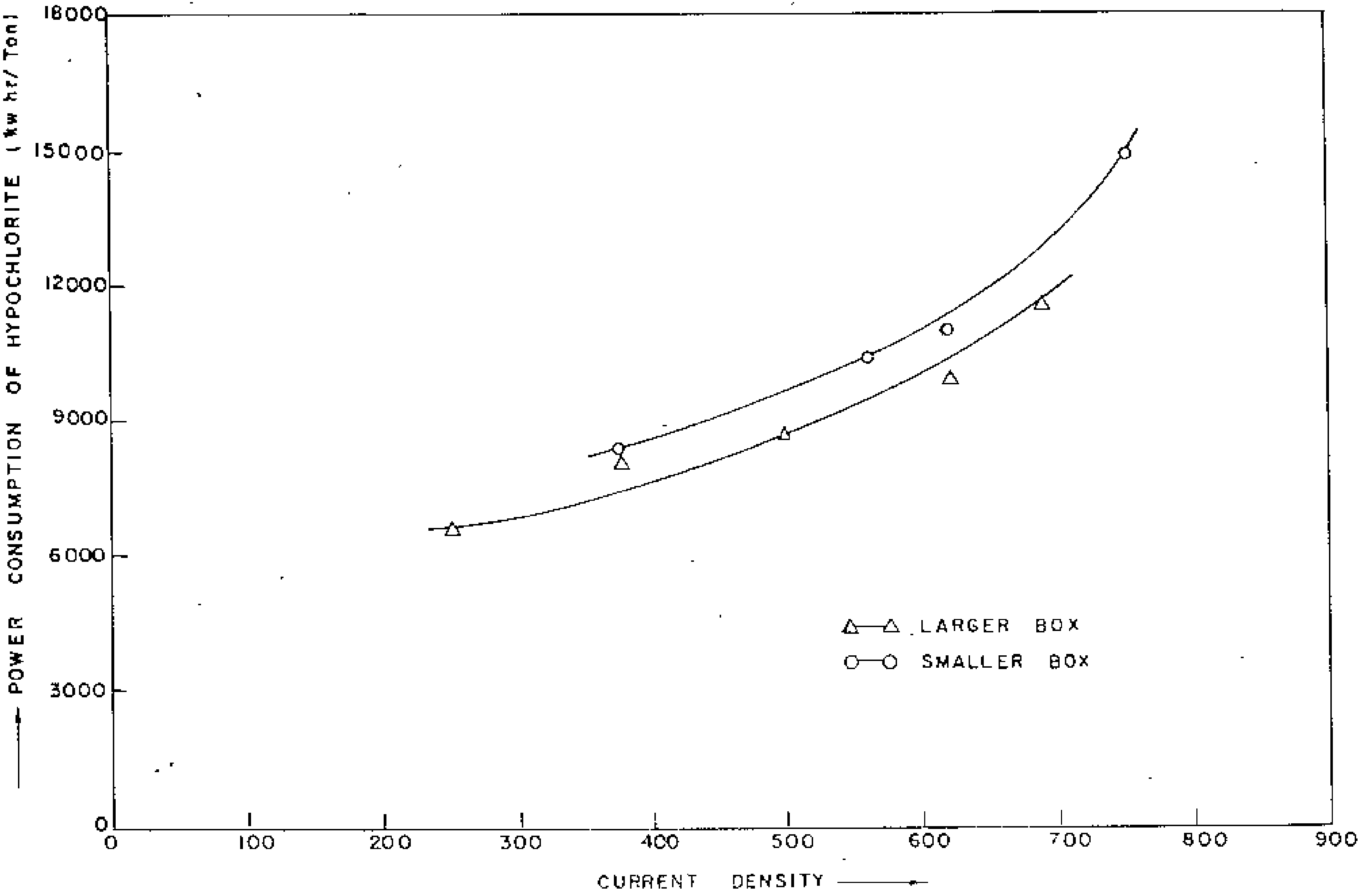


FIG. 3.18 VARIATION OF POWER CONSUMPTION WITH CURRENT DENSITY

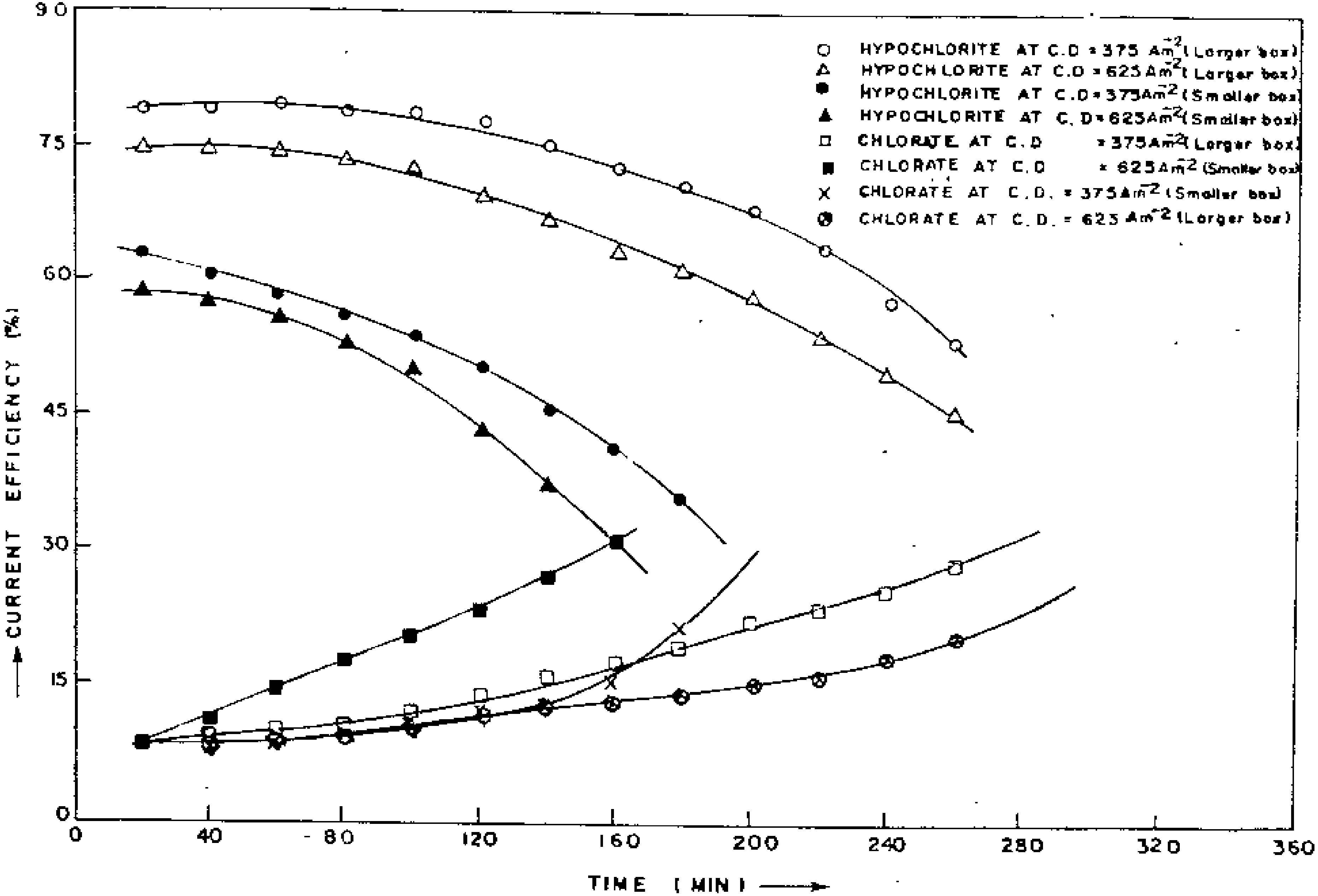


FIG. 3.19 VARIATION OF CURRENT EFFICIENCY FOR DIFFERENT SIZE OF EXPT. BOXES.

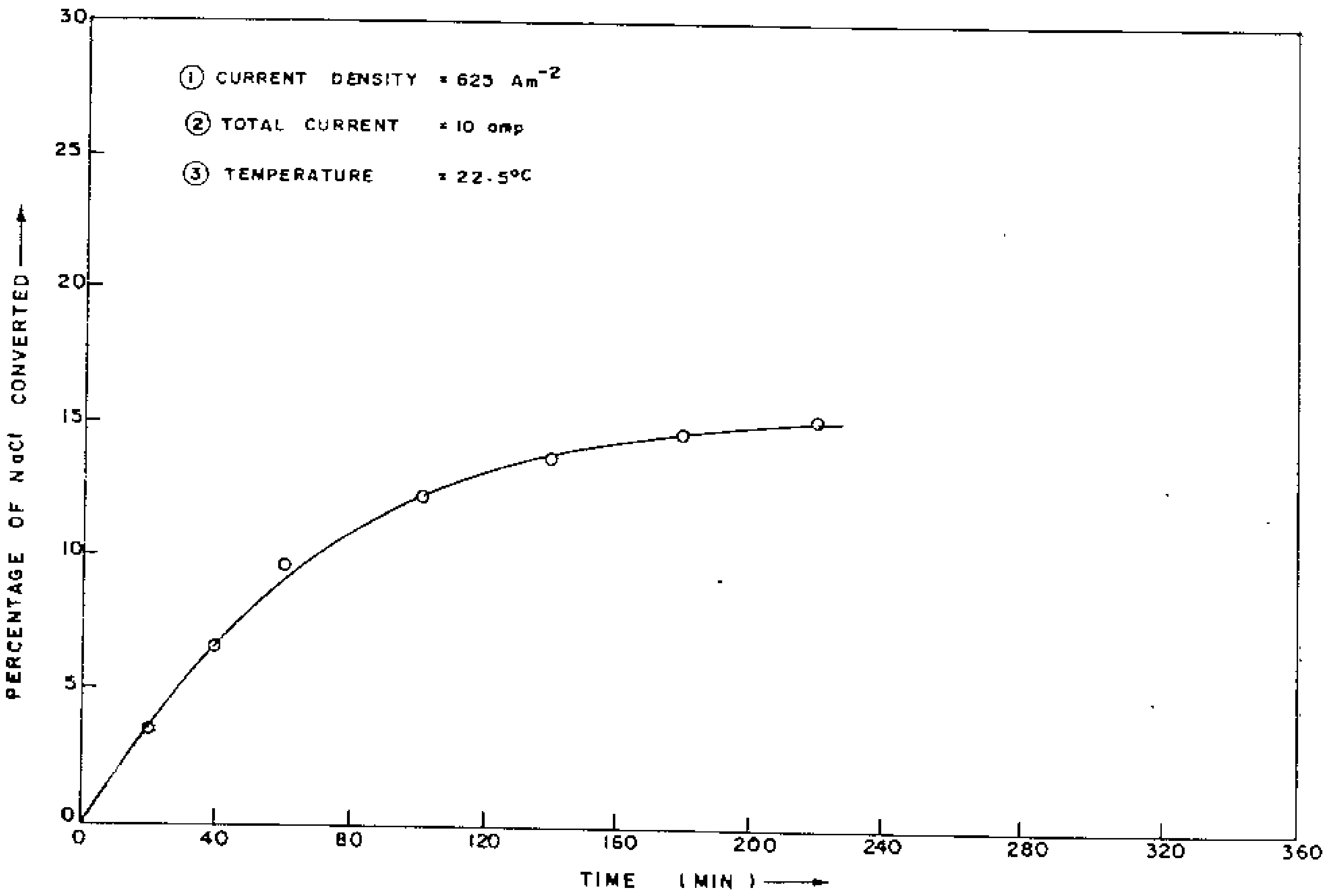


FIG. 3.20 VARIATION OF SODIUM CHLORIDE CONVERSION WITH TIME.

3.9 THE EFFECT OF CONCENTRATION OF ELECTROLYTIC SOLUTION.

The concentration of sodium chloride solution was varied from 0.5M to 4.0M during the experiments. It was difficult to obtain a solution having a concentration greater than 4.0M at the working temperature. At low concentration of sodium chloride solution(0.5M), initially the production of hypochlorite and current efficiency were high and almost equal to that of 4.0M sodium chloride solntion but after a short period of time the production and current efficiency were found to decrease rapidly,(Appendix,Table. 22). This may be attributed to the rapid deplotion of available sodium chloride in the cell.

It may be mentioned here that the above concentration of sodium chloride (4.0M) has been recognized for the optimum production of hypochlorite industrially[8,10,21] at the same working temperature range.

3.10 THE EFFECT OF THE NUMBER OF ELECTROLYTIC CELLS.

In the present investigation it has been found that the production of hypochlorite decreases with the decrease of the number of electrolytic cell used under the same experimental condition, but the current efficiency remains almost constant.

3.11 STORAGE OF HYPOCHLORITE

Hypochlorite is stored in a dark coloured glass stoppered bottle. When it is stored in a white glass bottle about 98.2% of hypochlorites are decomposed within 9 days. If it is stored in a dark coloured glass stoppered bottle, the decomposition of hypochlorite has been found to be around 16.59% within the same period. The rate of decomposition of hypochlorite and formation of chlorate stored in a dark blue coloured glass stoppered bottle are shown in table 3.3.

TABLE 3.3 DECOMPOSITION OF HYPOCHLORITE AND FORMATION OF CHLORATE STORED IN A DARK BLUE COLOURED GLASS STOPPERED BOTTLE.

Time in days	Hypochlorite			Chlorate		
	OCl^-/L (gm)	Decomposition. (gm)	Decomposition. (%)	ClO_3^-/L (gm)	Formation (gm)	Formation (%)
0	6.0692	x	x	3.1103	x	x
9	5.062	1.0072	16.59	3.3989	0.2886	9.27
40	3.8509	2.2183	36.54	3.5783	0.468	15.04
85	2.483	3.5862	59.08	3.6158	0.5055	16.25

CONCLUSION

(i) A novel electrochemical cell system was devised using graphite anode and stainless steel cathode for the optimum production of hypochlorite by the electrolysis of sodium chloride solution.

(ii) The cell is of simple geometric shape, ease of design and can be easily constructed. The cell box was closed so that hypochlorite can be easily formed in the cell from evolved chlorine gas at the anode and OH^- ions at the cathode.

(iii) The performance of the cell for hypochlorite production was assessed in terms of current efficiency, power consumption and space time yield.

(iv) The maximum current efficiency obtained in this investigation was 90.70% at current density of 625 Am^{-2} at 22°C using dichromate and the minimum power consumption was found to be 6882.66 KWhr/ton for hypochlorite production in this case. The maximum yield of hypochlorite obtained was 3.221gm/L.

APPENDIX

TABULATED EXPERIMENTAL RESULTS

TABLE 1. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AT C. D. 187.5 Am^{-2}.

(1) Total current = 3 amp.
(2) Voltage = 5 volts.
(3) Total soln. in the cell = 6 litres.
(4) Initial temperature = 23°C.
(5) pH = 7.01

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ (0.00854N) in ml required for OCl^-	OCl7L (gm)	Current efficiency (%)	Space time yield. (kgh^{-1} m^{-3})
15	20	9.30	0.1018	84.88	15.27
30	20	18.55	0.2031	84.63	15.23
45	20	27.85	0.3049	84.71	15.24
60	20	36.85	0.4035	84.06	15.13
75	20	45.50	0.5005	83.41	15.01
90	20	54.80	0.6000	83.34	15.00
105	20	63.60	0.6960	82.85	14.91
120	20	71.20	0.7832	81.58	14.68
135	20	78.40	0.8620	79.85	14.36
150	20	84.40	0.9221	77.37	13.86
165	20	89.00	0.9785	74.13	13.34
180	20	93.50	1.0285	71.42	12.85
205	20	95.90	1.054	64.29	11.56
220	20	96.50	1.0615	60.30	10.85

TABLE 2. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AT C.D. 187.5 Am^{-2}.

(1) Total current = 3 amp.
(2) Voltage = 5 volts.
(3) Total soln. in the cell = 7 litres.
(4) Initial temperature = 22°C
(5) pH = 9.10

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ ('oo714N) required for OCl^- (ml)	OCl^-/L (gm)	OCl^- (m.equiv/L)	Current efficiency (%)	Space time yield. (kgh^{-1} m^{-2})
5	20	3.25	0.029	1.14	86.04	15.48
20	20	12.90	0.118	4.60	86.53	15.55
35	20	22.40	0.205	7.99	85.77	15.41
50	20	32.10	0.295	11.45	86.04	15.48
65	20	41.30	0.379	14.73	85.15	15.32
80	20	50.05	0.459	17.86	83.84	15.07
95	20	58.90	0.541	21.04	83.18	14.96
110	20	68.00	0.624	24.26	82.84	14.90
125	20	75.60	0.695	27.00	81.14	14.60
140	20	84.20	0.773	30.05	80.60	14.50
155	20	91.90	0.844	32.79	79.46	14.30
170	20	98.10	0.900	35.01	77.33	13.89
200	20	110.50	1.015	39.43	74.04	13.32
240	20	125.00	1.148	44.61	69.80	12.56

TABLE 3. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AT C.D. 250 Am^{-2}.

(1) Total current = 4 amp.
(2) Voltage = 5 volts.
(3) Total soln. in the cell = 7 litres.
(4) pH = 6.5
(5) Initial temperature = 23.5°C

Time of electrolysis (min)	Volume of eloctrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ ('00735N) required for OCl^- (ml)	OCl^-/L (gm)	OCl^-/L (m.equiv/L)	Current efficiency (%)	Space time yield. (kgh^{-1} m^{-3})
20	20	15.60	0.1476	5.73	80.74	19.37
40	20	31.30	0.2963	11.50	80.09	19.44
60	20	46.70	0.4420	17.16	80.57	19.33
80	20	61.60	0.5825	22.63	79.66	19.11
100	20	75.60	0.7155	27.78	78.26	18.78
120	20	91.20	0.8630	33.51	78.67	18.87
140	20	104.00	0.9840	38.21	76.90	18.45
160	20	117.00	1.1070	44.99	75.69	18.16
180	20	128.60	1.2170	47.26	73.96	17.74
200	20	138.00	1.305	50.69	71.39	17.80
220	20	144.65	1.365	53.00	68.06	16.28
240	20	155.05	1.465	56.89	66.88	16.02
260	20	162.00	1.530	59.41	64.45	15.45
280	20	166.65	1.577	61.24	61.16	14.78

TABLE 4. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 375 Am^{-2}.

(1) Total current = 6 amp.
(2) Voltage = 6 volts.
(3) Total soln. in the cell = 7 litres.
(4) Initial temperature = 23°C
(5) pH = 7.20

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ soln. (0.0865N) required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	20	2.00	0.20	8.64	0.86	81.26	8.11	29.19	1.57
40	20	3.95	0.45	17.08	1.94	80.16	9.13	28.86	1.77
60	20	5.95	0.80	25.76	3.46	80.64	10.82	29.01	2.10
80	20	7.90	1.20	34.17	5.19	80.16	12.17	28.86	2.36
100	20	9.80	1.55	42.39	6.70	79.55	12.58	28.65	2.44
120	20	11.55	1.95	49.96	8.43	78.13	13.19	28.13	2.56
140	20	13.20	2.45	57.10	10.60	76.53	14.20	27.56	2.76
160	20	15.00	3.00	64.89	12.98	76.10	15.22	27.41	2.96
180	20	16.60	3.70	71.81	16.00	74.86	16.68	26.96	3.24
200	20	17.80	4.40	77.00	19.03	72.24	17.86	26.02	3.47
220	20	19.05	5.30	82.41	22.93	70.29	19.55	25.31	3.80
240	20	20.00	6.60	86.52	28.55	67.64	22.32	24.36	4.34

TABLE 5. POWER CONSUMPTION OF HYPOCHLORITE AT C.D. 375 Am^{-2}.

(1) Total current = 6 amp.
(2) Voltage = 6 volts.
(3) Total soln. in the cell = 7 litres.
(4) Initial temperature = 22°C
(5) pH = 7.10

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ (0.0855N) required for OCl^-	OCl^-/L. (gm)	Total OCl^- (gm)	Power consumption (KWhr/Ton)
20	20	1.95	0.217	1.520	7892.14
40	20	3.90	0.434	3.041	7892.14
60	20	5.90	0.657	4.600	7825.22
80	20	7.75	0.863	6.043	7943.06
100	20	9.65	1.075	7.525	7973.42
120	20	11.50	1.281	8.967	8028.98
140	20	12.85	1.431	10.020	8383.22
160	20	14.25	1.587	11.111	8639.68
180	20	15.60	1.737	12.164	8878.28
200	20	16.55	1.843	12.905	9298.36
220	20	17.15	1.910	13.373	9870.26
240	20	17.20	1.916	13.412	10736.24
260	20	17.05	1.899	13.295	11733.28

TABLE 6. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 375 Am^{-2}.

(1) Total current = 6 amp.
(2) Voltage = 6 volts.
(3) Total soln. in the cell = 7 litres.
(4) pH = 9.1
(5) Initial temperature = 22.5°C

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ soln. ('08656N) required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	20	2.05	0.20	8.86	0.86	83.20	8.11	29.97	1.58
40	20	4.05	0.45	17.52	1.94	82.19	9.13	29.60	1.77
60	20	6.10	0.75	26.38	3.24	82.53	10.14	29.72	1.97
80	20	8.15	1.10	35.25	4.75	82.70	11.16	29.79	2.17
100	20	10.05	1.50	43.47	6.49	81.58	12.17	29.38	2.37
120	20	11.90	1.90	51.48	8.22	80.50	12.85	28.99	2.50
140	20	13.65	2.25	59.05	9.73	79.14	13.04	28.51	2.54
160	20	15.30	2.65	66.19	11.45	77.62	13.45	27.96	2.61
180	20	17.10	3.30	73.97	14.26	77.11	14.89	27.78	2.89
200	20	18.30	3.90	79.16	16.76	74.27	15.84	26.75	3.08
220	20	19.50	4.60	84.36	19.88	71.95	16.98	25.92	3.30
240	20	20.00	5.35	86.52	23.14	67.64	18.09	24.36	3.52
260	20	20.05	6.90	86.74	29.85	62.60	21.57	22.55	4.19

TABLE 7. PRODUCTION,CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 375 Am^{-2}(SMALLER BOX).

(1) Total current = 6 amp.
(2) Voltage = 5 volts.
(3) Total soln. in the cell = 1.5 litres.
(4) Initial temperature = 32.5°C
(5) pH = 9.1

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ soln ('08771N) required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. ($kgh^{-1}\ m^{-3}$)	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	10	3.55	0.55	3.12	4.82	62.59	9.70	22.54	1.88
40	10	6.85	1.20	60.06	10.52	60.38	10.58	21.75	2.05
60	10	9.90	2.10	86.81	18.41	58.17	12.34	20.95	2.40
80	10	12.60	3.05	110.51	26.74	55.55	13.44	20.00	2.61
100	10	15.15	4.40	132.87	38.58	53.43	15.52	19.24	3.02
120	10	17.00	6.10	149.10	53.49	49.96	17.93	17.99	3.48
140	10	18.00	8.10	157.87	71.03	45.34	20.40	16.33	3.97
160	10	18.60	10.40	162.88	91.20	40.93	22.92	14.76	4.46
180	10	18.00	12.80	157.89	112.25	35.25	25.08	12.70	4.88

TABLE 8. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 500 Am^{-2}.

(1) Total current = 8 amp.
(2) Voltage = 6 volts.
(3) Total soln. in the cell = 7.6 litres.
(4) Initial temperature = 23°C
(5) pH = 9.10

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ soln. ('08822N) required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	20	2.30	0.25	10.14	1.10	77.50	8.42	37.21	2.18
40	20	4.55	0.55	20.06	2.42	76.66	9.26	36.81	2.40
60	20	6.85	0.85	30.20	3.74	76.94	9.54	36.94	2.47
80	20	9.05	1.30	39.90	5.73	76.23	10.95	36.60	2.84
100	20	11.15	1.80	49.16	7.93	75.14	12.13	36.08	3.14
120	20	13.00	2.55	57.32	11.24	73.01	14.32	35.05	3.71
140	20	14.50	3.60	63.94	15.87	69.80	17.33	33.51	4.49
180	20	16.55	6.00	72.98	26.46	61.96	22.46	29.75	5.83
220	20	16.95	8.35	74.74	36.83	51.92	25.58	24.43	6.63
260	20	16.00	11.05	70.55	48.73	41.47	28.64	19.91	7.43

TABLE 9. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 562.5 Am^{-2}.

(1) Total current = 9 amp.
(2) Voltage = 6.5 volts.
(3) Total soln. in the cell = 7 litres.
(4) pH = 9.2
(5) Initial temperature = 22°C

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ soln. (0.0662N) required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	20	2.85	0.30	12.27	1.29	76.82	8.08	41.50	2.36
40	20	5.65	0.70	24.34	3.01	76.15	9.43	41.13	2.75
60	20	8.35	1.10	35.97	4.73	75.03	9.88	40.53	2.88
80	20	10.85	1.60	46.72	6.89	73.08	10.72	39.49	3.14
100	20	13.20	2.25	56.87	9.69	71.16	12.17	38.44	3.54
120	20	14.95	3.05	64.41	13.14	67.16	13.70	36.28	4.00
160	20	18.20	4.80	78.41	20.68	61.32	16.17	33.12	4.72
200	20	20.45	7.20	88.11	31.02	55.12	19.40	29.77	5.66
240	20	21.30	11.10	91.77	47.82	47.84	24.93	25.84	7.28

TABLE 10. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 562.5 Am^{-2} WITH THE ADDITION OF DICHROMATE.

(1) Total current = 9 amp.
(2) Voltage = 6 volts.
(3) Total soln.in the cell = 7 litres.
(4) Amount of dichromate added = 2.5 gm/L.
(5) Initial temperature = 22°C
(6) pH = 9.2

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ soln. (0.0862N) required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	20	3.35	0.25	14.43	1.07	90.30	6.73	48.78	1.96
40	20	6.65	0.60	28.65	2.58	89.63	8.08	48.41	2.36
60	20	9.90	0.95	42.09	4.09	88.96	8.53	48.05	2.49
80	20	12.95	1.50	55.79	6.46	87.27	10.10	47.14	2.95
100	20	15.80	2.20	68.07	9.47	85.18	11.85	46.01	3.46
120	20	18.30	3.05	78.84	13.14	82.22	13.70	44.41	4.00
140	20	20.40	3.90	87.89	16.80	78.56	15.01	42.43	4.38
180	20	23.40	6.35	100.82	27.36	70.00	19.01	37.86	5.56
220	20	25.30	9.80	109.01	42.22	62.00	24.01	33.49	7.01
260	20	25.05	13.25	107.93	57.09	51.94	27.47	28.06	8.02

TABLE 11. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 625 Am^{-2} WITH THE ADDITION OF DICHROMATE.

(1) Total current = 10 amp.
(2) Voltage = 6 volts.
(3) Total soln. in the cell = 7.6 litres.
(4) Amount of dichromate added = 2.5 gm/L.
(5) pH = 9.2
(6) Initial temperature = 31°C.

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ soln. ('090N) required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	10	1.60	0.125	14.40	1.12	88.00	6.87	52.83	2.23
40	10	3.20	0.30	28.80	2.70	88.00	8.25	52.83	2.67
60	10	4.75	0.50	42.75	4.50	87.09	9.16	52.28	2.97
80	10	6.25	0.85	56.25	7.96	85.94	11.69	51.60	3.80
100	10	7.65	1.10	68.85	9.90	84.15	12.10	50.52	3.93
120	10	8.80	1.60	79.20	14.40	80.67	14.67	48.43	4.77
160	10	10.80	2.40	97.20	21.60	74.25	16.50	44.58	5.36
200	10	12.40	3.40	111.69	30.60	68.26	18.70	40.95	6.08
240	10	13.70	4.95	123.30	44.55	62.79	22.69	37.70	7.38
280	10	13.80	6.60	124.20	59.40	54.22	25.93	32.55	8.43

TABLE 12. POWER CONSUMPTION FOR HYPOCHLORITE PRODUCTION AT C. D. 625 Am^{-2}.

(1) Total current = 10 amp.
(2) Voltage = 7 volts.
(3) Total soln. in the cell = 8.30 litres.
(4) Initial temperature = 22.5°C
(5) pH = 7.15

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ soln. (0.0913N) required for OCl^-	OCl^-/L (gm)	Total production of OCl^- (gm)	Power consumption. (KWhr/Ton)
20	20	2.45	0.2879	2.390	9762.84
40	20	4.90	0.5759	4.780	9762.84
60	20	7.30	0.8580	7.121	9830.02
80	20	9.60	1.1285	9.366	9964.52
100	20	11.85	1.3929	11.561	10090.90
120	20	13.60	1.5986	13.268	10551.24
140	20	15.30	1.7985	14.927	10941.70
160	20	16.55	1.9454	16.147	11560.38
180	20	18.05	2.1217	17.6105	11924.46
200	20	19.05	2.2393	18.586	12554.18
220	20	19.45	2.2863	18.976	13525.76
240	20	19.50	2.2922	19.025	14717.38

TABLE 13. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 625 Am^{-2}.

(1) Total current = 10 amp.
(2) Voltage = 6 volts.
(3) Total soln. in the cell = 7.6 litres.
(4) Amount of dichromate added = 2.5 gm/L.
(5) pH = 9.1
(6) Initial temperature = 22°C

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ soln. (0.090N) required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	10	1.65	0.125	14.85	1.12	90.76	6.87	54.49	2.23
40	10	3.25	0.30	29.25	2.70	89.38	8.25	53.99	2.67
60	10	4.80	0.50	43.20	4.50	88.00	9.16	52.83	2.97
80	10	6.35	0.75	57.15	6.75	87.32	10.32	52.42	3.34
100	10	7.80	1.00	70.02	9.00	85.80	11.00	51.51	3.56
120	10	9.00	1.45	81.00	13.06	82.50	13.30	49.53	4.31
160	10	11.10	2.10	99.90	18.91	76.32	14.42	45.82	4.68
200	10	12.80	3.05	115.20	27.41	70.40	16.79	42.27	5.44
240	10	13.75	4.55	123.75	40.53	63.02	20.64	37.84	6.76
280	10	13.90	6.15	125.10	55.40	54.61	24.18	32.78	7.84

TABLE 14. POWER CONSUMPTION FOR HYPOCHLORITE PRODUCTION AT C. D. 625 Am^{-2} WITH THE ADDITION OF DICHROMATE.

(1) Total current = 10 amp.
2) Voltage = 6 volts.
(3) Total soln. in the cell = 7.6 litres.
(4) Amount of dichromate added= 2.5 gm/L.
(5) pH = 9.2
(6) Initial temperature = 22°C

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ soln. ('090N) required for OCl^-	OCl^-/L (gm)	Total production of OCl^- (gm)	Power consumption for OCl^- (KWhr/Ton)
20	10	1.65	0.3823	2.9058	6882.66
40	10	3.25	0.7531	5.724	6988.12
60	10	4.80	1.1124	8.454	7097.22
80	10	6.35	1.4716	11.184	7153.06
100	10	7.80	1.8076	13.738	7279.02
120	10	9.00	2.0857	15.851	7570.16
160	10	11.10	2.5724	19.55	8184.14
200	10	12.80	2.9664	22.544	8871.30
240	10	13.75	3.1865	24.217	9910.08
280	10	13.90	3.2213	24.4818	11437.04

TABLE 15. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 562.5 Am^{-2} (SMALLER BOX).

(1) Total current = 9 amp
(2) Voltage = 6 volts.
(3) Total soln.in the cell = 1.5 litres.
(4) Initial temperature = 32°C
(5) pH = 9.06

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ soln. ('0862N) required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
10	10	2.60	0.30	22.41	2.58	60.09	6.9	32.45	2.02
30	10	7.00	1.05	60.33	9.05	53.92	8.08	29.12	2.36
50	10	11.45	2.35	98.67	20.24	52.92	10.86	29.59	3.17
70	10	15.70	4.30	135.33	37.06	51.837	14.14	28.00	4.14
90	10	17.75	6.70	152.99	57.75	45.58	17.20	24.62	5.02
110	10	20.10	9.90	173.26	83.61	42.23	20.37	22.81	5.95
130	10	21.50	12.80	185.32	110.33	38.22	22.75	20.64	6.64
150	10	22.00	17.50	189.63	150.85	33.90	26.96	18.31	7.87
170	10	20.90	21.70	180.15	187.05	28.41	29.498	15.34	8.61
190	10	19.90	26.60	171.53	229.29	24.20	32.35	13.07	9.44

TABLE 16. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 625 Am^{-2} (SMALLER BOX).

(1) Total current = 10 amp.
(2) Voltage = 6 volts.
(3) Total soln. in the cell = 1.70 litres.
(4) Initial temperature = 33°C
(5) pH = 9.05

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ ('090N) soln. required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	10	4.75	0.65	42.75	5.90	58.44	8.07	35.08	2.59
40	10	9.40	1.70	84.60	15.45	57.82	10.56	34.71	3.39
60	10	13.40	3.40	121.79	30.90	55.50	14.08	33.00	4.52
80	10	16.90	5.55	153.60	50.44	52.50	17.24	31.21	5.53
100	10	20.05	8.10	182.24	73.62	49.82	20.13	29.62	6.46
120	10	20.85	10.90	189.51	99.07	43.18	22.57	25.66	7.25
140	10	20.90	14.75	189.96	134.07	37.10	26.18	22.05	8.41
160	10	20.05	19.35	182.24	175.88	31.14	30.06	17.86	9.65

TABLE 17. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 625 Am^{-2} WITH THE ADDITION OF DICHROMATE (SMALLER BOX).

(1)	Total current	=	10 amp.
(2)	Voltage	=	6 volts.
(3)	Total soln. in the cell	=	1.56 litres
(4)	Amount of dichromate added	=	2.5 gm/L.
(5)	Initial temperature	=	33°C
(6)	pH	=	9.6

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ soln. ('08928N) required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	10	5.70	0.85	50.87	7.58	63.82	9.52	38.32	3.08
40	10	11.25	1.90	100.44	16.96	63.00	10.64	37.81	3.45
60	10	16.70	3.20	149.10	28.57	62.35	11.94	37.42	3.87
80	10	19.65	5.25	175.40	46.87	55.01	14.70	33.02	4.76
100	10	20.60	8.00	183.92	71.42	46.14	17.92	27.69	5.81
140	10	23.95	17.00	213.82	151.77	38.32	27.20	23.00	8.82
180	10	23.20	33.20	207.13	296.41	28.87	41.32	17.33	13.40
220	10	21.20	48.15	189.27	429.89	21.58	49.03	12.95	15.90

TABLE 18. PRODUCTION,CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 625 Am^{-2} USING PURE (E.MERCK) NaCl CHLORIDE(SMALLER BOX).

(1) Total current = 10 amp.
(2) Voltage = 6 volts.
(3) Total soln. in the cell = 1.55 litres.
(4) Initial temperature = 23°C
(5) pH = 7.05

Time of electrlysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ ('0847N) soln. required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	10	7.00	0.90	59.28	7.62	73.90	9.50	44.36	3.08
40	10	13.95	2.05	118.15	17.36	73.63	10.82	44.21	3.51
60	10	20.20	3.75	171.09	31.77	71.08	13.20	42.67	4.28
80	10	25.10	6.60	212.59	55.92	66.24	17.42	39.77	5.65
100	10	28.10	10.40	238.00	88.11	59.33	21.97	35.62	7.12
120	10	29.90	14.00	253.25	118.62	52.61	24.64	31.58	8.00
140	10	30.50	17.90	258.33	151.66	53.66	27.01	27.61	8.76

TABLE 19. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 750 Am^{-2} (SMALLER BOX)

(1) Total current = 12 amp

(2) Voltage = 8 volts.

(3) Total soln. in the cell = 1.6 litres.

(4) Initial temperature = 22°C

(5) pH = 9.15

Time of electrlysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ ('08403N) soln. required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	10	6.45	0.90	54.19	7.56	58.11	8.10	41.86	3.15
40	10	12.85	1.90	107.96	15.96	57.88	8.56	41.70	3.33
60	10	18.90	3.20	158.79	26.88	56.76	9.61	40.89	3.74
80	10	23.60	5.10	198.28	42.85	53.15	11.48	38.29	4.47
100	10	26.75	8.00	224.75	67.22	48.18	14.41	34.72	5.61
120	10	30.20	12.30	253.73	103.34	45.34	18.47	32.66	7.19
140	10	31.60	16.50	265.50	138.60	40.67	21.23	29.29	8.26
160	10	31.70	22.00	266.34	184.85	35.70	24.77	25.71	9.64
180	10	30.40	29.20	255.42	245.53	30.43	29.23	21.92	11.38

TABLE 20. PRODUCTION,CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 750 Am^{-2} WITH THE ADDITION OF DICHROMATE (SMALLER BOX).

(1) Total current = 12 amp.
(2) Voltage = 8 volts.
(3) Total soln. in the cell = 1.56 litres.
(4) Amount of dichromate added = 2.5 gm/L.
(5) Initial temperature = 22.5°C
(6) pH = 9.15

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ soln. ('0892N) required for		Concentration (m.equiv/L.)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	10	6.35	1.00	56.69	8.92	59.27	9.33	42.69	3.63
40	10	12.65	2.15	112.94	19.19	59.04	10.03	42.52	3.90
60	10	18.75	3.60	167.40	32.14	58.34	11.20	42.01	4.36
80	10	21.40	5.90	191.06	52.67	49.94	13.76	35.96	5.35
100	10	23.15	9.00	206.68	80.35	43.22	16.80	31.12	6.54
140	10	26.95	19.10	240.61	170.52	35.93	25.46	25.88	9.91
180	10	26.10	37.30	233.01	333.01	27.07	38.68	19.49	15.06
220	10	23.85	53.80	212.93	480.33	20.23	45.65	14.57	17.77

TABLE 21. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 750 Am^{-2} (SMALLER BOX).

(1) Total current = 12 amp.
(2) Voltage = 8 volts.
(3) Total soln. in the cell = 1.6 litres.
(4) Initial temperature = 33°C
(5) pH = 9.15

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ ('08403N) soln. required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	10	6.20	0.95	52.09	7.98	55.86	8.58	40.24	3.33
40	10	12.30	2.20	103.34	18.48	55.41	9.91	39.91	3.85
60	10	17.70	3.80	148.71	31.92	53.15	11.41	38.29	4.44
80	10	21.80	6.70	183.16	56.29	49.10	15.09	35.37	5.87
100	10	25.85	10.70	217.19	89.90	46.58	19.28	33.55	7.50
120	10	28.20	15.10	236.96	121.87	42.34	22.67	30.50	8.82
140	10	28.90	19.10	242.81	160.48	37.19	24.58	26.79	9.57
160	10	28.00	25.95	235.25	218.04	31.53	29.22	22.71	11.37
180	10	26.90	32.35	226.01	271.81	26.92	32.38	19.39	12.61

TABLE 22. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 625 Am^{-2} USING 0.5M SODIUM CHLORIDE SOLUTION (SMALLER BOX).

(1) Total current = 10 amp.
(2) Voltage = 7 volts.
(3) Total solution in the cell = 1.80 litres.
(4) Initial temperature = 33°C
(5) pH = 9.10

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ (0.090N) soln. required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	10	4.45	0.70	40.04	6.30	57.96	9.11	34.79	2.95
40	10	8.60	1.50	77.38	13.50	56.00	9.77	33.62	3.16
60	10	12.20	2.50	109.77	22.50	52.96	10.85	31.79	3.52
80	10	15.00	3.75	134.97	33.75	48.84	12.21	29.32	3.96
100	10	17.00	5.60	152.96	50.40	44.28	14.59	26.58	4.73
120	10	18.30	7.95	164.66	71.55	39.72	17.26	23.85	5.59
140	10	18.80	10.80	169.16	97.20	34.98	20.10	21.00	6.52
180	10	17.10	18.50	153.86	166.51	24.74	26.77	14.85	8.68

TABLE 23. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 625 Am^{-2} (LARGER BOX).

(1) Total current = 5 amp.
(2) Voltage = 5.5 volts.
(3) Total solution in the cell = 7.00 litres.
(4) Total number of cells = 4
(5) Initial temperature = 23°C
(6) pH = 9.10

Time of electrolysis (min)	Volume of $Na_2S_2O_3$ (0.0865N) soln. required for	Volume of $Na_2S_2O_3$ (0.0865N) soln. required for		Concentration (m. equiv/L).		Current efficiency (%)		Space time yield. (kgh^{-1} m^{-3})	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	20	1.65	0.15	7.13	0.64	80.33	7.30	24.11	1.18
40	20	3.30	0.35	14.27	1.51	80.33	8.52	24.11	1.38
60	20	4.90	0.55	21.19	2.37	79.52	8.92	23.87	1.44
80	20	6.55	0.80	28.32	3.45	79.72	9.73	23.93	1.57
100	20	8.15	1.05	35.24	4.53	79.36	10.22	23.82	1.65
120	20	9.60	1.40	41.51	6.04	77.90	11.36	23.38	1.84
140	20	10.95	2.00	47.35	8.64	76.16	13.91	22.86	2.25
160	20	12.15	2.55	52.54	11.01	73.94	15.52	22.20	2.51
180	20	13.30	3.35	57.51	14.47	71.95	18.12	21.60	2.94
200	20	14.05	4.30	60.76	18.57	68.40	20.93	20.53	3.39
220	20	14.90	5.40	64.43	23.33	65.95	23.90	19.79	3.87
260	20	15.05	7.80	65.08	33.70	56.36	29.21	16.92	4.73

TABLE 24. PRODUCTION, CURRENT EFFICIENCY AND SPACE TIME YIELD OF HYPOCHLORITE AND CHLORATE AT C.D. 687.5 Am^{-2}.

(1) Total current = 11 amp.
(2) Voltage = 7.5 volts.
(3) Total soln. in the cell = 7.5 litres.
(4) Initial temperature = 32°C
(5) pH = 9.04

Time of electrolysis (min)	Volume of electrolytic soln. analysed (ml)	Volume of $Na_2S_2O_3$ (0.0854N) soln. required for		Concentration (m.equiv/L)		Current efficiency (%)		Space time yield. ($kgh^{-1}\ m^{-3}$)	
		OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-	OCl^-	ClO_3^-
20	20	3.10	0.40	13.23	1.70	72.58	9.36	47.93	3.34
40	20	6.15	0.85	26.25	3.62	71.99	9.95	47.54	3.55
60	20	9.30	1.30	39.71	5.55	72.57	10.14	47.93	3.62
80	20	12.30	1.70	52.51	7.47	71.99	10.24	47.54	3.55
100	20	15.35	2.25	65.54	9.60	71.88	10.53	47.46	3.75
120	20	17.60	3.15	75.15	13.44	68.67	12.29	45.35	4.38
140	20	19.45	4.10	83.04	17.50	65.05	13.71	42.96	4.89
160	20	21.35	5.20	91.16	22.20	62.47	15.21	41.25	5.43
180	20	23.05	6.40	98.42	27.32	59.95	16.64	39.59	5.94
200	20	24.35	7.80	103.97	33.30	57.00	18.26	37.64	6.51
220	20	24.80	9.10	105.89	38.85	52.77	19.36	34.85	6.91
260	20	23.90	12.25	102.05	52.30	43.03	22.61	28.42	7.87

BIBLIOGRAPHY

1. Foerster, F. : Trans. Am. Electrochem. Soc. 46,23-50 (1924).

2. Anon : Chem. & Met.Eng. 51,130-3 (1944).

3. Schumacher, J.C. : Chem. & Met. Eng. 51,108-9,130-3, (December,1944).

4. Sproesser : Z. Elektrochem. 7,971-76,987-94, 1027-35,1071-76,1083-93,(1901).

5. Linari, A. & Pietra, V.L. : Chimia-o-Industria(Italy) 19,693-6 (1937).

6. Groggins, P. H. : Chem. & Met. Eng. 44,302-7(1937).

7. Pitman, A. L. with Groggins, P. H. : Trans. Electrochem. Soc. 79,93-109 (1941).

8. IBL, N. and Landolt, D. : J. Electrochem. Soc. 115, 713 (1968).

9. Mueller, E. : Z. Electrochem. 5,469(1899).

10. Ali, M.S. : M.Sc. Thesis, University of Newcastle Upon Tyne, England, (1974).

11. Hammer, L. and Wranglen, G. : Electrochem. Acta 9,(1964).

12. Nagai, T. and Takei, T. : J. Electrochem. Soc. Japan, 25,373 (1957).

13. Nagai, T. and Takei, T. : Denki Kagaku, 25,517(1957).

14. Goodridge, F. and King, C.J. H. : " Techniques of Electro organic synthesis ". Chapter 2.

15. Pink,C.G & Pan,L.C. : Trans. Electrochem. Soc.49, 85 (1926).

16. Western, P. G. & Hooglan,J. G. : Electrochem. Technol.5,56 (1967).

17. Eberil,V.I.,Kokulina, L.I,Elina,L.M,Krishtalik, L. I. : Electrokhymia,5(3),336(1969).

18. Bauer,R. : Chem. Ing. Tech. 34,Nr5, 376(1962).

19. Udupa,H.V.K,Sampath,S. Narashiman,K.C. Sundarajan,S.Raju,C.J, Chandran,T.J.V, Natarajan,S.etc. : Indian Journal of Technology 4,305 (1966).

20. Katzon,I.S.& Sokolov, P.I. : J.Appl. Chem. (U.S.S.R.),5, 902 (1932).

21. Janens,M. : Trans. Electrochem. Soc. 92, 23 (1947).

22. Matsamura,T, Itair, Shibuya,M & Ishi,G. : Electrochemical Technology. 6,902 (1932).

23. Udupa,H.V.K & Narasimhan,K.C. : Indian Pat. 66,195,22 Dec,1958.

24. Sugino,K. & Shibasaki,Y : J.Electrochem,Soc. Japan, 16,(1948),9.

25. Sugino,K. : Bull.Chem.Soc.Japan,23 (1950),115.

26. Narasimhan,K.C, Sundara Rajan,S.& Udupa,H.V.K. : J. Electrochem. Soc. 108(1961) 798.

27. Nagalingam,M, Thiagarajanin Govinda, Rao. P, & Udupa. : Chem. ages Bombay,16(1965)491.

28. Fleck,J. : Chem. Ing. Tech,43(4),173(1971).

29. Grubs,G & Burkharot,A. : Z. electrochem,30,67(1924).

30. Liebreich, E. : Z. electrochem. 30,344(1924).

31. Wielderholt,W. : Z. electrochem. 30,263(1924).

32. Jaksic,M. M; Nikolich, B, & Karanovic,D. M. : U. S. 3,597,337(1971).

33. Westar land, G. O. : Can. Pat. 76169(1968).

34. BRD-Auslege Schrift. : 1279665(1968),Daiki. Eng. Co. Ltd. Tokyo.

35. Wester lund, G.O. : East German Pat.55,935. (To Chemec. Eng. Ltd).

36. Kelsall, G. H. : Journal of Applied Electrochemistry 14(1984)177-186.