

Hydrogen Production by The Electrolysis of Saline Water

by

IbnelWaleed Ali Hussein

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

May, 1992

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Hydrogen production by the electrolysis of saline water

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King Fahd University of Petroleum and Minerals (Saudi Arabia), 1992

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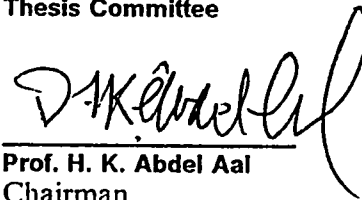
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MASTER OF SCIENCE IN CHEMICAL ENGINEERING

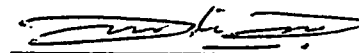
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this thesis is dedicated to my parents

ABSTRACT

In this research, the electrolysis of sea water is carried out for the production of hydrogen. Natural as well as synthetic sea water with a concentration of 0.14 - 2 times that of sea water is electrolyzed. A modified Hoffman electrolysis cell is used. Both electric energy (DC) and solar energy are used to electrolyze the water .

A number of parameters are investigated including current density, voltage, and quantity of electricity in the range of : 25 - 126 mA/ cm^2 , 6 - 20 V, and 500 - 1500 C respectively . Their effects on the cell performance are studied and reported as follows.

Hydrogen is produced at a current efficiency of 99% . Its production is current density dependent, and increases with the salinity (T.D.S) for a given voltage. Precipitates consisting mainly of $Mg(OH)_2$, are formed at the cathode and their rate of formation is found to be proportional to T.D.S. Samples of the precipitate are analyzed and results are reported.

Chlorine on the other hand, results at the anode. Typical molar ratios for hydrogen, chlorine and oxygen obtained for sea water in the range of 500 - 1500 C are:- $H_2 / Total Cl_2$ is 1.2 - 1.4, $H_2 / (Cl_2 \text{ in gas phase})$ is 7 - 215, Cl_2 / O_2 is 3 - 4.6. Similar results for other salinities are reported in the text.

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الخلاصة

فى هذا البحث ، تمت دراسة عملية التحليل الكهربائى لماء البحر لإنتاج الهيدروجين . وقد إستعملت كلا من مياه البحر الطبيعية وكذلك المياه التى تم تحضيرها فى المعمل بتركيز من ١٤ إلى ضعف تركيز ماء البحر . وقد استخدم جهاز (هوفمان) المطور تحت تأثير التيار الكهربائى المباشر بالإضافة الى التيار الناتج عن الخلايا الشمسية (الضوئية) .

تم بحث تأثير عدد من العوامل والتى تتضمن كثافة شدة التيار ، الفولت ، وكمية الكهرباء فى المدى من ٢٥ - ١٢٦ م أمبير/سم^٢ ، ٦-٢٠ فولت ، و ٥٠٠ - ١٥٠٠ كولم على التوالي . وقد كانت اهم النتائج هي :

انتاج الهيدروجين بكفاءة شدة تيار ٩٩٪ مع ازدياد الانتاج بزيادة كثافة شدة التيار . وكذلك يزداد انتاج الهيدروجين اثناء ثبات الفولت مع زيادة الملوحة ولقد وجد أن هيدروكسيد الماغنيسيوم يترسب على القطب السالب ويزداد الترسيب مع زيادة الملوحة كما هو موضح فى نتائج الرسالة .

ومن الناحية الأخرى تصاعد غاز الكلور على القطب الموجب ووجد أن النسبة بين مولات الهيدروجين ، الكلور والاكسجين لماء البحر فى المدى ٥٠٠ - ١٥٠٠ كولم هي كالتالى : الهيدروجين / الكلور الكلى من ١٢ - ١٤ ، الهيدروجين/ الكلور فى الحالة الغازية من ٧-٢١٥ ، الكلور/ الاكسجين من ٢-٤٦ وقد ضمننت نتائج مماثله لدرجات الملوحة الأخرى فى نص هذا البحث .

CHAPTER ONE
INTRODUCTION

CHAPTER ONE

INTRODUCTION

Hydrogen is a clean fuel which is easily transported and stored. It has the highest gravimetric energy density of all known fuels (e.g. hydrogen has 142 kJ/g compared to 56 kJ/g for methane)

Alkaline water electrolysis is the technology in present practice for large-scale electrolytic hydrogen production. Low efficiency, low current density, and a lack of proper scale-up practice are the primary drawbacks of the present technology. Significant improvements have been made possible to reach improved cell efficiency and high current densities. Many advanced concepts relating to various aspects of electrolytic hydrogen production are reported in the literature.

The alkaline water electrolysis uses fresh water with low salt content, and hence additional treatment and desalination systems add to the cost of hydrogen produced. Figure 1.1 shows two established technologies of electrolysis, the alkaline water electrolysis and the brine electrolysis. In the former hydrogen is the main product while in the latter caustic soda and chlorine are the primary products and hydrogen is a by-product. The cell for fresh water electrolysis is known as H_2 / O_2 cell while for saturated brine electrolysis, it is an H_2 / Cl_2 cell. Hydrogen/oxygen is produced in the ratio of 2:1 in the former cell, while hydrogen/

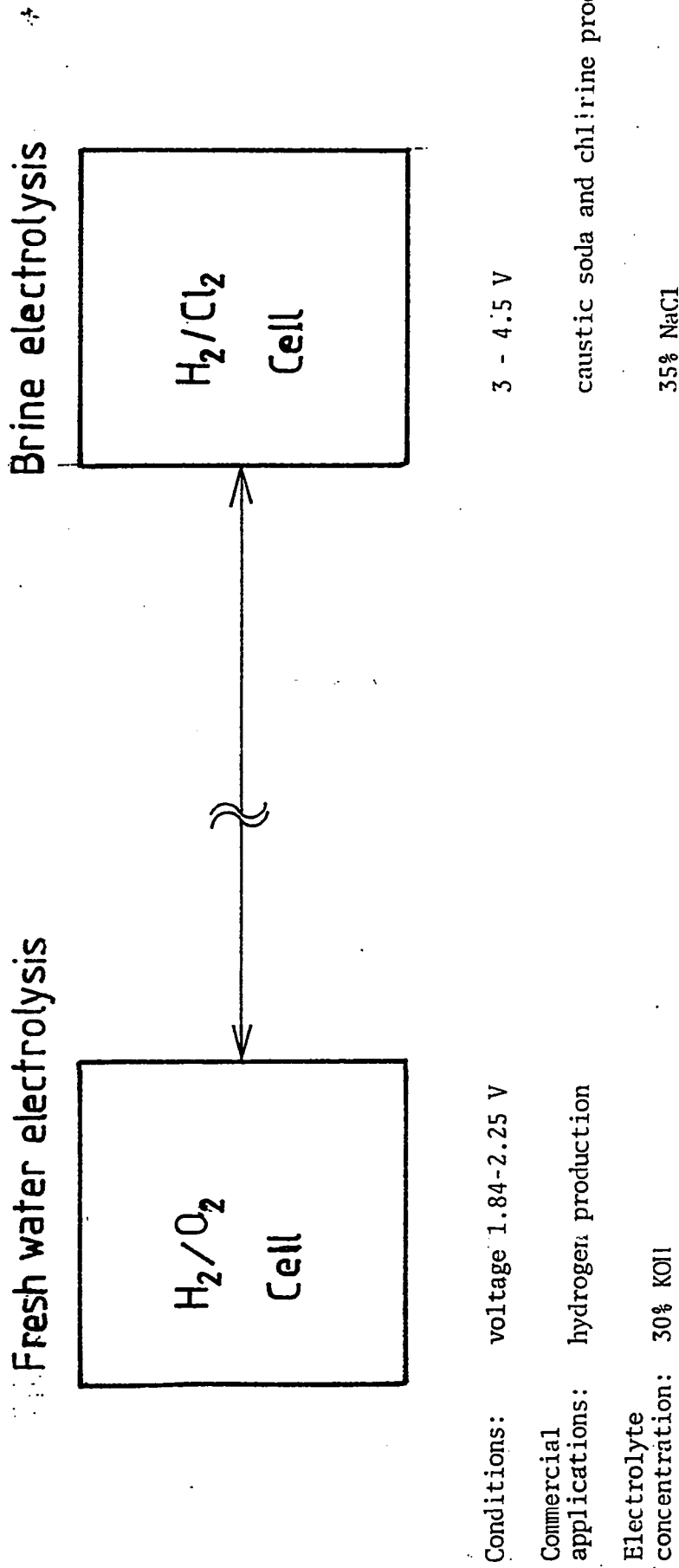


Fig. 1.1 Established technology of electrolysis.

chlorine is produced in the molar ratio of 1:1 in the latter as shown in Figure 1.2.

The salinity range between 3000 ppm and 300,000 ppm is still a potential area of reseach. This range is found in sea water which is the most abundant source of hydrogen.

This investigation cosiders electrolysis of natural and synthetic sea waters in the range of 0.5 - 7 % TDS with the following main objectives :

- (i) To review the literature on hydrogen production by the electrolysis of fresh and saline waters.
- (ii) To study the effect of salinity, voltage, current, and quantity of electricity on hydrogen production in modified Hoffman cell.
- (iii) To study the effect of the above parameters on chlorine evolution.
- (iv) To evaluate the cell performance with respect to the precipitate formed on the cathode.

A comparison of alkaline water electrolysis, brine electrolysis and sea water eelectrolysis is shown in Table 1.1 .

One of the most promising applications of the current as well as future electrolyzer technologies is to use solar photovoltaic to generate the power needed for electrolysis. Solar energy was simulated in this work by a DC power supply operated at different conditions of voltage and current. In addition to few runs carried out using solar energy input.

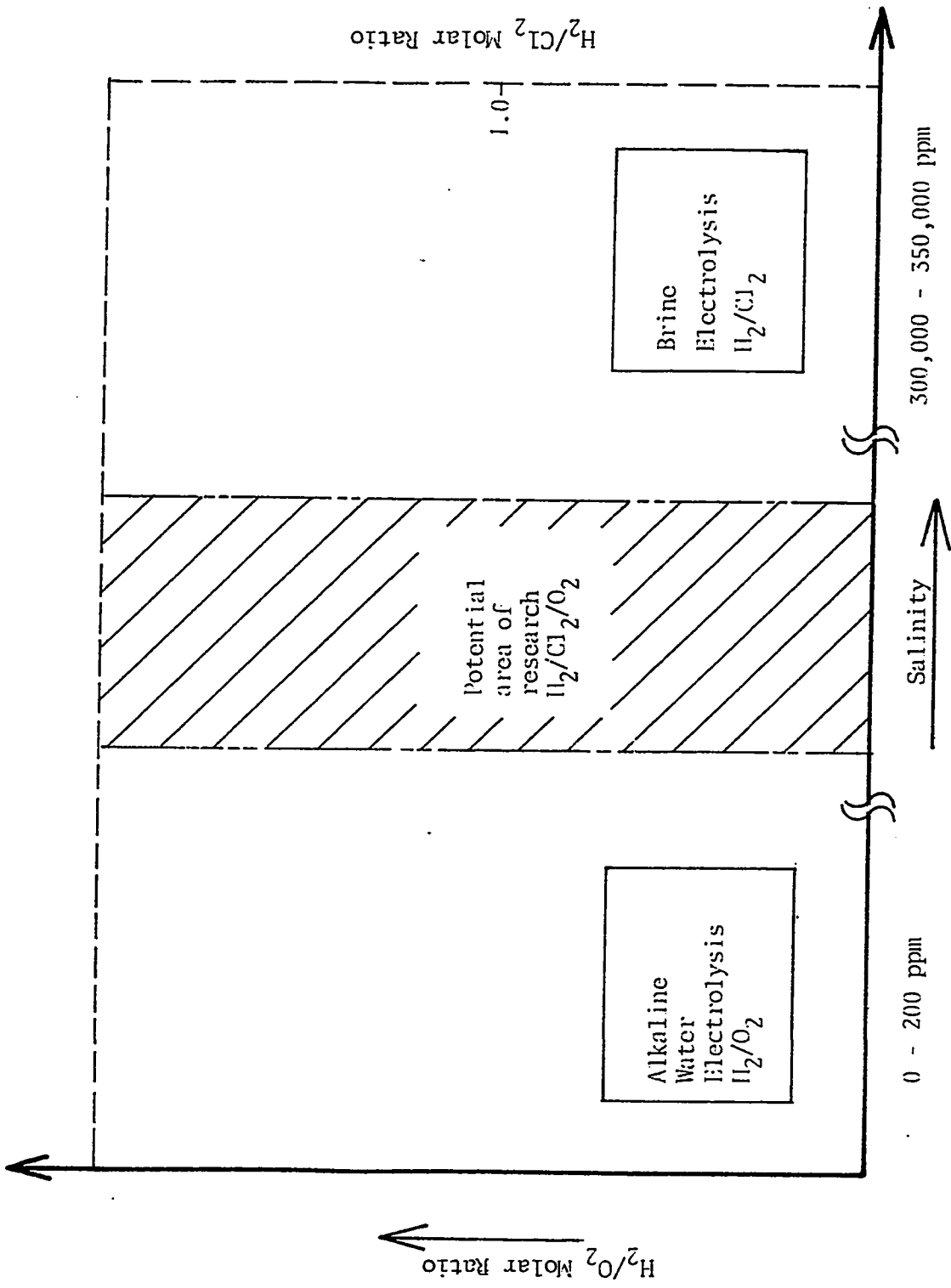


Fig. 1.2 Established technology of electrolysis vs. saline water electrolysis.

Table 1.1 Fresh and saline water electrolysis at a glance

Technology	Conventional Fresh Water Electrolysis	Brine Electrolysis	Sea Water Electrolysis
Development Stage	Commercial Large Scale Units	Commercial Large Scale Units	Very Small Laboratory Scale
Cell Voltage, V	1.84 - 2.25	3.0 - 4.5	> 2.1
Decomposition Voltage, V	1.47	2.31	1.8 - 2.2
Current	130 -250 (mA/cm ²)	150 - 200 kA/day	25 - 126 (mA/cm ²)
Temperature, °c	70 - 90	60 - 70	23 - 25
Cathode	nickel, steel stainless steel	Ti coated with Pt	Pt
Anode	Ni	graphite,Ti	Pt
Cell Type	H ₂ /O ₂	H ₂ /Cl ₂	H ₂ /(Cl ₂ /O ₂)
Electrolyte	25-35 % KOH	NaCl	sea water + drops of HCl
Salinity Level	200 - 400 ppm	35% w	3.4% w
Chlorine Current Efficiency	-	95-97%	75-82%
Main Product(s)	H ₂	Cl ₂ , NaOH	H ₂
By Product(s)	O ₂	H ₂	Cl ₂ , NaOCl
Major Advantage	Proven technology Simple	Proven technology	Low cost
Disadvantage	-Low efficiency -Low current density -High production cost -Corrosive electrolyte	Low efficiency	Within lab. scale

Previous problems associated with chlorine analysis by iodometry (end point detection with thiosulfate) and usual difficulties encountered with gas sampling for a GC were avoided by the use of ascorbic acid (vitamin C) for the oxidation/reduction reaction between ascorbic acid and iodine as explained in chapter three.

Hydrogen and chlorine production rates at different conditions of voltage and current densities as well as precipitate formation are discussed in chapter four.

Conclusions drawn from this study and recommendations for further work are detailed in chapter five .

CHAPTER TWO
LITERATURE SURVEY

CHAPTER TWO

LITERATURE SURVEY

2.1 INTRODUCTION

Hydrogen is an important raw material for the synthesis of chemical compounds, for processing mineral oil , and is an essential fuel for space transportation . Hydrogen has the highest gravimetric energy density of all known fuels .

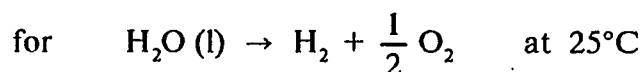
Experience has shown that hydrogen gas will not present any problems of transportation, distribution, and utilization as a source of thermal energy. As a motor vehicle fuel, whether as gas at room temperatures or liquid stored at cryogenic temperatures, hydrogen has the characteristics which make it meet all the normal transportation fuel requirements. For the most part it is free from pollutants, with the exception of NO_x .

Other fuels have no particular safety advantages if compared with hydrogen. Hydrogen is neither toxic nor radioactive , and thus will not be the cause of any long-term damages . But hydrogen / oxidizer mixtures have a relatively wide ignition range; it only require a small amount of energy to ignite, and tend to propagate rapidly, especially in enclosed rooms. Because hydrogen has high diffusivity in air, and lighter in weight inflammable mixtures dilute rapidly or burn out quickly.

2.2 THERMODYNAMICS OF WATER DECOMPOSITION

The process of water decomposition by electrolysis is the reverse process of hydrogen combustion. Therefore, the theoretical amount of energy required per unit mole of hydrogen produced is the same as the heat of combustion . Each hydrogen molecule is formed by the addition of two electrons to two hydrogen ions in solution, so that a direct relation exists between the current passed (the electron flow rate) and the rate of hydrogen production (Faraday's Law) . Deviations from Faraday's law are characterized by the electric-current efficiency of the cell.

2.2.1 Effect of Temperature on The Electrochemical Production of Hydrogen



$$\Delta G^\circ = -56.69 \text{ kcal/mol}$$

$$\Delta H = 68.32 \text{ kcal/mol}$$

$$\Delta S^\circ = 39.13 \text{ kcal/mol K}$$

$$E^\circ (1 \text{ atm}) = 1.229 \text{ V}$$

In electrolysis, only the free energy of reaction, ΔG , can be interchanged with electrical energy at constant temperature and pressure. The quantity of electric charge corresponding to the molar quantities indicated in the balanced chemical equation is nF , where n is the number of electrons transferred per molecule and F is the Faraday value. If this quantity of electrical charge is transported through a potential difference of E volts, the amount of work required is

given by nFE . Because this electrical change does not involve mechanical work and is carried out isothermally, the change in Gibbs free energy is given by :

$$\Delta G = -nFE \quad (2-1)$$

where E is the potential difference, or voltage, which is by convention is taken as positive. If ΔG is negative for a spontaneous cell reaction and E is taken as positive for a spontaneously discharging cell, there results a negative sign in Eqn. 2-1. The free-energy-change voltage, E , or "reversible voltage" for water electrolysis is calculated, by substituting $\Delta G^\circ = -56.69 \text{ kcal/mol}$, in Eqn. 2-1. The value of the reversible voltage, E° , is then 1.23 V .

The entropy change for an electrolytic-cell reaction may be calculated from the temperature coefficient of the electromotive force as follows :

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$$

Substitute this relation into Eqn. 2-1

$$nF \left(\frac{\partial E}{\partial T}\right)_p = \Delta S \quad (2-2)$$

The temperature coefficient of the standard reversible potential is given by⁽¹⁾ :

$$\left(\frac{\partial E}{\partial T}\right) = 0.25 \text{ mV}/^\circ\text{C}$$

Hence, as the temperature rises, the voltage which must be applied to a cell to overcome the thermodynamically necessary energy is reduced. The enthalpy change for the cell reaction is given by :

$$\Delta H = \Delta G + T\Delta S \quad (2-3)$$

and substituting for the values of ΔG and ΔS using equations (2-1) and (2-2) to obtain :

$$\Delta H = -nFE + nFT \left(\frac{\partial E}{\partial T} \right)_p \quad (2-4)$$

Eqn. 2-4 shows that the difference between the free-energy change and the total-energy change (enthalpy) is equal to the entropy change in the process. The entropy change is an irreversibility (i.e. loss). In a hypothetical reversible process $\Delta S=0$ then $\Delta G= \Delta H$, and the voltage corresponding to the enthalpy change of 68.32 kcal/mol is calculated from Eqn. 2-1, as 1.47 V at 25°C. Under these hypothetical conditions, hydrogen is produced entirely by using electricity, and there is no thermal energy transfer between the system and the surrounding. This voltage is called the "thermoneutral potential"⁽²⁾.

In practical cells, there is usually a voltage drop which is greater than the difference between the free-energy voltage and the enthalpy voltage. In other words, practical cells usually operate at voltages greater than 1.47 V and liberate heat. The heat required to supply the energy for this reaction is therefore provided by some of the above liberated heat, and practical cells do not absorb heat from their surroundings. If a 100% efficient cell could be operated at a

voltage below 1.47 V, it would act as a refrigerator, drawing heat from its surroundings to make up the deficit in the energy input. There seems to be little chance of developing electrolytic cells that operate so close to the ideal that they do, in fact, act as refrigerators. However, there seems to be a reasonable chance of obtaining cell operation at 1.47 V, which would represent an apparent 100% conversion of electrical energy to the fuel value of hydrogen. If such a cell performance can be achieved an apparent efficiency of 100% is demonstrated. This would still represent an electrochemical efficiency of only 83%. It is curious, therefore, that a practical device could probably be produced that operates at an apparent efficiency of 100% without violating the basic laws of thermodynamics. This operation voltage of 1.47 V is a good target to aim for in the development of advanced electrolytic cells⁽³⁾.

As shown in Figure 2.1 The reversible voltage varies inversely with the temperature of the solution, i.e. raising the temperature lowers the voltage at which water can be decomposed. This factor works in favor of the electrolysis cells because at higher temperatures the electrode reaction proceeds faster, with less losses, while the required energy input is less. This is in contrast to fuel cells; their available energy output falls as the temperature is raised. The thermoneutral voltage, on the other hand, varies only slightly with temperature from 1.47 V at 25°C to 1.50 V at 340°C. This is shown in Figure 2.1

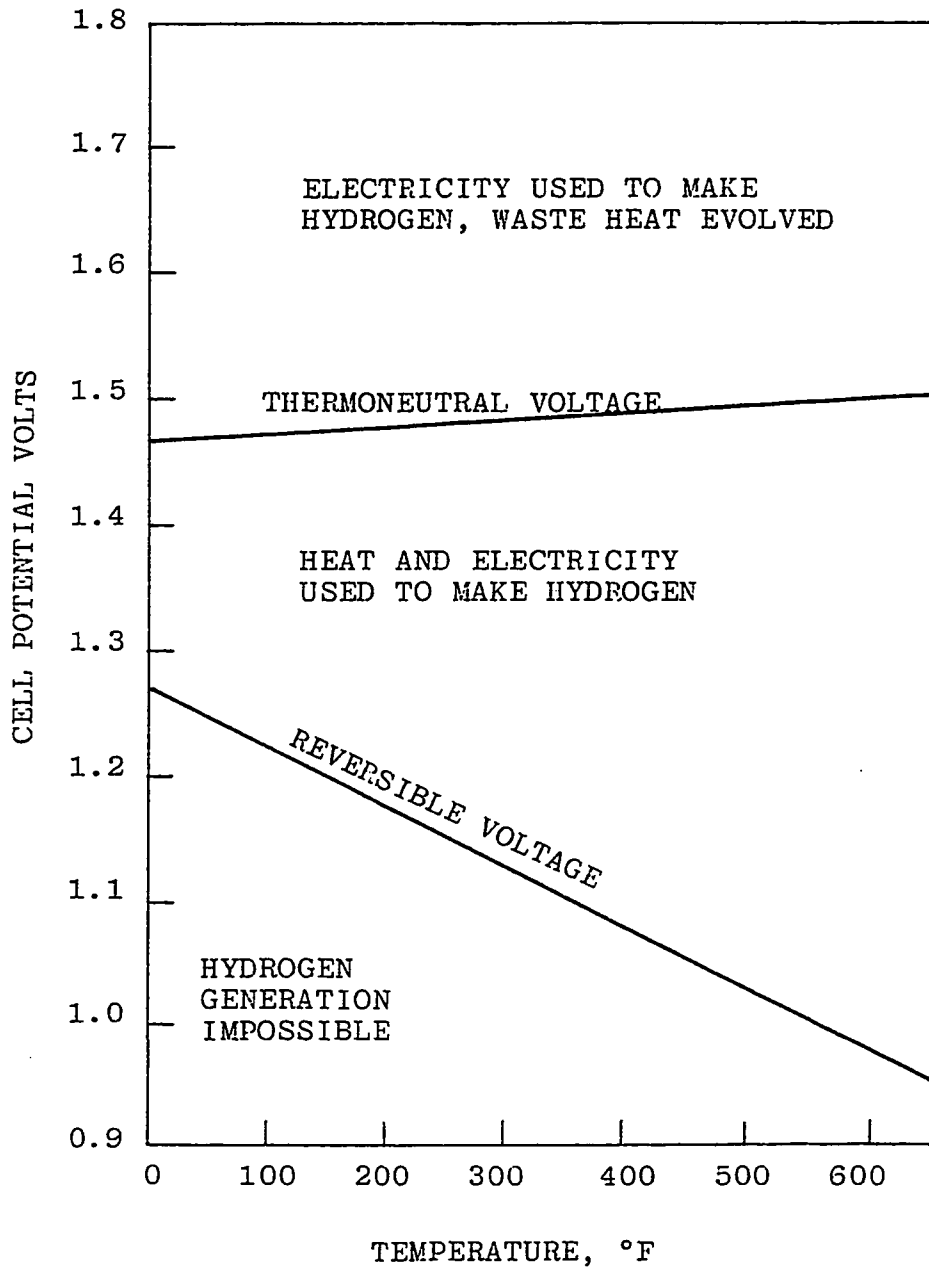


Fig. 2.1. Idealized operating conditions for electrolyzer(3).

2.2.2 Effect of Pressure on Decomposition Voltage

In considering the theoretical aspects of the effect of pressure on electrolysis, the effect of pressure on the decomposition voltage and on the efficiency of the cell must be studied first. During electrolysis, the free-energy change can be written as :

$$dG = -SdT + VdP \quad (2-5)$$

If this is applied at constant temperature, the partial derivative form of Eqn. 2-5 w.r.t P is given by :

$$\frac{\partial G_p}{\partial P} - \frac{\partial G_r}{\partial P} = V_p - V_r \quad (2-6)$$

where G_r , G_p , V_r , and V_p are Gibbs free energies and volumes of the reactants and products, respectively. This equation may be written as :

$$\frac{\partial \Delta G}{\partial P} = \Delta V \quad (2-7)$$

where ΔV is the change in volume during reaction. Substituting for the value of ΔG using Eqn. 2-1, we get :-

$$\frac{\partial E}{\partial P} = -\frac{\Delta V}{nF} \quad (2-8)$$

Assuming that the volume of the liquid water is small compared with that of gaseous products, and further assuming the volumes of these gases obey the perfect gas law

$$PV = ZRT \quad (2-9)$$

where Z = number of moles

Eqn. 2-10 is obtained

$$dE = \left(\frac{ZRT}{nF} \frac{dP}{P} \right)_{O_2} + \left(\frac{ZRT}{nF} \frac{dP}{P} \right)_{H_2} \quad (2-10)$$

Integrating the above equation between ambient conditions (25° C , 1 atm) and the operating pressure, gives :

$$E_p = E^\circ + \frac{0.052}{2} \log P_{H_2} + \frac{0.058}{4} \log P_{H_2} \quad (2-11)$$

Since $P_{H_2} = P_{O_2}$ during electrolysis, equation (2-11) is simplified to the form :

$$E_p = E^\circ + 0.0435 \log P \quad (P \text{ in atm}) \quad (2-12)$$

Thus, raising the pressure of operation of a water electrolyzer results in a theoretical increase in the decomposition voltage of 43 mV for every tenfold increase in pressure. The energy required to provide this additional voltage is exactly equal to the potential energy contained in the high-pressure hydrogen. In practice, electrolyzer cells have higher efficiencies at atmospheric pressure. The main reason is that at high pressure the gas bubbles evolved are less and provide less hindrance to passage of ionic current across the cell. The energy requirements of a practical cell are always greater than the minimum theoretical energy requirements described above.

Efficiency losses occur because of

- (a) the resistance of the electrolyte itself.
- (b) changes in the voltage of the electrodes due to concentration polarization.
- (c) voltage gradients set up at the electrode-electrolyte interface itself due to the slowness of the electrode reactions.

There are also small losses in the electronic conduction of current through the metal parts of the cell.

Because a practical cell operates at a higher voltage than the theoretical value of 1.23 V (at room temperature and pressure), the difference between the actual applied voltage and the theoretical voltage is commonly called overvoltage. The change in voltage at individual electrodes is often called polarization, and the terms overpotential and polarization are used synonymously. The voltage efficiency of the cell can be determined by comparing the actual operating voltage with the theoretical voltage at the operating conditions. The operating voltage of a cell varies according to the current that is passed through it. Just as in an ohmic resistance, increasing the current results in an increase in voltage. If the operating voltage of the cell is plotted against the current per unit area of electrode, commonly termed the current density, a characteristic curve, called a polarization curve, is obtained. This curve is considered to be a vital parameter in the design of an electrolyzer system because it shows the relationship between voltage efficiency and the current density for the rate of hydrogen production (a

typical polarogram is shown in chapter 4. Clearly, by doubling the rate of current density, and thus doubling the hydrogen-production rate, the effective capital cost of the cell is halved, although efficiency is penalized. The polarization curve can be used to show a trade-off between capital cost and efficiency in determining an optimum operation point⁽³⁾.

In practical cells, high current efficiencies, approaching 100%, are usually achieved because there is usually no other path for the current to take. When multiple cells are connected together in series and use a common electrolyte, some current can short-circuit from one end of the cell stack to the other through the electrolyte feed channels. This only occurs with certain cell designs and results in a slight loss of current efficiency. Another source of efficiency loss is the recombination of hydrogen and oxygen because they dissolve to some extent in the electrolyte and crossover into the separator. This loss becomes more pronounced when cells are operated at high pressures because of the increase in solubility. In practical low-pressure cells current efficiencies in excess of 98% are usually obtained. The energy efficiency, or power efficiency, of a cell is, therefore, largely dependent upon the voltage losses or polarization of the cell, which remains the most important characteristic in determining the energy requirements for the practical electrolytic cell.

2.3 BASIC DESIGNS OF ELECTROLYZER CELLS

2.3.1 Types of Electrolyzer Cells

Water electrolyzers are generally classified according to two constructional techniques : tank-type (conventional) electrolyzers and filter press (bipolar) electrolyzers.

A single tank-type cell usually contains a number of electrodes, and all electrodes of the same polarity are connected in parallel, as shown in Figure 2.2 . Tank-type electrolyzer is usually operated at low voltage (1.9 - 2.5 V DC) and high current densities (0.5 - 1.0 A cm⁻²) . There are two major advantages to tank type electrolyzers:

- (i) Relatively few parts are required to build a tank-type electrolyzer, and those parts that are needed are relatively inexpensive. Because of this feature, tank-type electrolyzers tend to optimize at a lower thermal efficiency than do more sophisticated electrolyzer structures. Therefore tank-type electrolyzers are usually selected when electric-power costs are at their lowest.
- (ii) Individual cells may be isolated for repair or replaced simply by short-circuiting the two adjacent cells with a bus bar. This feature allows maintenance to be carried out with a minimum of downtime for the entire plant.

The major disadvantages of tank-type electrolyzers are :

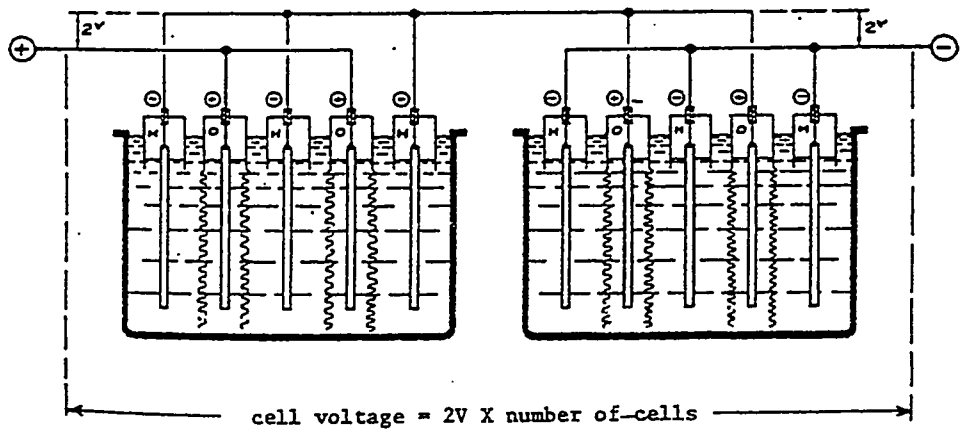


Fig. 2.2 Schematic diagram of a unipolar (tank - type) electrolyzer (3)

- (a) Their inability to operate at high temperatures because of heat losses from the large surface areas.
- (b) Their requirements for more floor space than other types of electrolyzers.
- (c) The difficulty of designing the tanks to operate at high pressures

On the other hand bipolar electrolyzers use stacks so that the positive electrode of one cell is directly connected to the negative electrode of the next. An assembly of cells has superficial resemblance to a filter press because the electrolyte is manifolded to flow through each cell in parallel while gases exit lines are similarly manifolded through the stack (see Figure 2.3). In practice, filter-press-type cells are usually constructed with separate electrodes in each cell that are electrically connected through a solid metal separator plate that serves to keep the hydrogen cavity of one cell separate from the oxygen cavity of the next. The major advantages of filter-press-type electrolyzers are that

- (i) They take up less floor space than the tank-type design.
- (ii) They are more amenable to operation at high pressures.

The major disadvantages are:

- (a) They require a much closer tolerance in construction because of sealing problems.
- (b) They are more difficult to maintain because if one cell fails, the entire battery has to be dismantled and production of hydrogen stopped.

Filter press electrolyzers usually present higher capital costs per unit area than tank-type cells, and, to compensate for this, they are operated at higher current

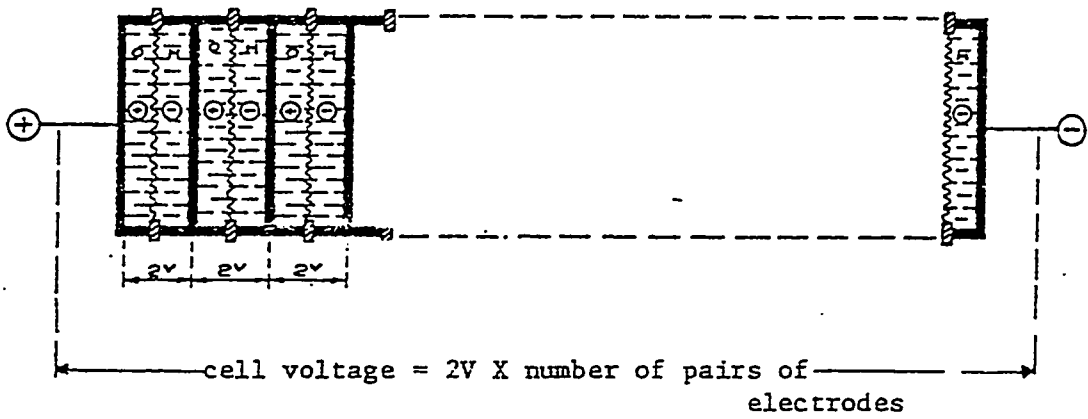


Fig. 2.3 Filter-press (bipolar) cell construction⁽⁴⁾

densities⁽⁴⁾ .

Cells that use a solid-polymer electrolyte (SPE) are usually constructed on the filter press-type design. They do not require electrolyte circulation because the electrolyte is immobilized in the form of an ion-exchange resin. The advantages of the solid-polymer type cell are :

- (i)The electrolyte membrane or diaphragm can be made very thin,allowing high conductivity without risk of gas crossover,
- (ii) The electrolyte is immobilized and cannot be leached out of the cell.

The disadvantages of the SPE cell are:

- (a) The electrolyte costs more than the conventional alkaline solutions.
- (b)The electrolyte is corrosive and requires more expensive metal components to be used in the cell.

For these reasons, SPE cells are usually operated at somewhat higher current densities than cells that use a liquid alkaline electrolyte.

One of the new approaches in electrolyzers design uses conventional aqueous alkaline electrolyte, but incorporates closely spaced, catalytic, porous electrodes and a thin asbestos paper separator. Another uses a solid-polymer acid type ion-exchange electrolyte; while the third one employes a solid-oxide ceramic electrolyte.

2.3.2. Innovations in Alkaline Water Electrolysis Technology

Zero-Gap Cell Geometry

The "Zero-Gap" electrode arrangement used in modern water electrolyzers generally requires perforated electrodes pressed onto the diaphragm from both sides, a technology first introduced more than 20 years ago in the Lurgi Electrolyzer⁽⁵⁾. In a zero-gap electrode arrangement, the gases evolve mostly on the electrode's back side i.e. the gas bubbles are collected on the side away from the diaphragm. Figure 2.4 demonstrates the principle of the zero-gap cell geometry. It also illustrates the fact that while the diameter of the mesh or perforated plate's holes should be as small as possible, they should match the average bubble size of the evolved gases to avoid the bubbles clogging the holes. For the cathode, a useful hole diameter is about 0.5 mm; because of the larger diameter of oxygen bubbles^(6,7) it is about 1mm for the anode⁽⁸⁾.

2.4 MATERIALS USED IN THE ELECTROLYSIS PROCESS

The most important materials used in the electrolysis process are the diaphragms, the electrolytes, and the electrodes. The following is an updated review on each of these materials.

2.4.1 Diaphragms

In order to maintain separation between the hydrogen generated at the cathode and the gases evolved at the adjacent anode, a diaphragm is inserted between the two electrodes. The diaphragm must be stable in caustic alkali solution and must minimize diffusion of the product gases without impeding ionic conductivity to prevent the passage of gas bubbles. The diaphragm must consist

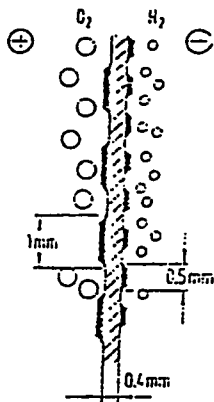


Fig. 2.4 Zero - gap cell geometry (7)

of small pores, the capillary pressure of which is greater than the maximum differential pressure applied across the cell. A woven asbestos cloth, artificial fiber cloth, rubber cloth or metallic net is usually employed as a diaphragm material. The most popular diaphragm is a bag or skirt of asbestos which is in some instances reinforced by cotton or wire. Under proper conditions, a diaphragm will last in excess of 20 years⁽⁹⁾. New diaphragms, made of composite materials, have better properties than the old. A comparison of separator materials is given by Casper⁽³⁾.

2.4.2 Electrolytes

In general, an aqueous solution of caustic potash or soda is used as the electrolyte for water electrolysis. At equal concentrations, the conductivity of caustic potash solutions is higher than that of caustic soda solution. The solubility of carbon dioxide, which contaminates the electrolyte and decreases its conductivity, is lower in caustic potash solution than in caustic soda solution. The conductivity lowering by absorbing the same amount of carbon dioxide is also smaller in the former. The highest conductivities are observed at the strengths of about 30% of caustic potash and about 20% of caustic soda. Though the conductivity of the electrolyte and the energy efficiency of water electrolysis increase as the temperature increases, the present clay water electrolysis cells are usually operated at 60 - 80°C for the caustic potash cell and at 50 - 70°C for the caustic soda cell, respectively, in order to reduce the consumption of electrolyzer materials. High purity water must be used to preserve the electrolysis cell operating characteristics.

2.4.3 Electrodes

Electrodes must have the following characteristics :

- (i) good electronic conductors.
- (ii) suitable catalytic surface for the discharge of hydrogen or hydroxyl ions.
- (iii) provide a large area interface between the catalyst and the electrolyte.
- (iv) provide adequate sites for the nucleation of gas bubbles
- (v) provide a reasonable means for the detachment of gas bubbles so that they may separate themselves from the electrolyte at the operating voltage of the cell.

The form of the electrodes varies considerably from one cell design to another. Large surface areas are obtained by the use of sintered structures, finned bodies, screens, perforated plates, and flat plates with electrochemically roughened surfaces. In the alkaline cells, nickel is the most commonly used catalytic surface. Rather than making electrodes out of solid nickel, nickel-plated mild steel is often used. A study on the performance of different nickel-plate metals made by deGiz⁽¹⁰⁾. The application of precious-metal catalysts, such as platinum, assists the electrode processes considerably and allows them to proceed more rapidly than on nickel. In the case of the polymeric acid electrolyte, electrodes must be made of more chemically resistant materials than nickel or steel. Tantalum and gold have been used, while the precious metals themselves, platinum, rhodium, iridium, etc. , are usually considered necessary as catalysts.

When platinum is used, a large surface area can be obtained by the use of so-called platinum black, a finely divided powder of platinum metal particles.

2.5 EFFICIENCIES OF WATER ELECTROLYSIS

2.5.1 Voltage Efficiency

In aqueous solution of caustic potash or soda, the reversible voltage of water electrolysis E_r is a direct function of the potential difference between the anode and the cathode and the logarithm of the ratio of P_{H_2O} , and $P_{H_2O}^{o(4)}$. The reversible voltage of water electrolysis E_r is then expressed by :

$$E_r = (E_a - E_c) - \frac{RT}{2F} \ln \left(\frac{P_{H_2O}}{P_{H_2O}^o} \right) \quad (2-13a)$$

where

E_r = reversible voltage

E_a and E_c = anode and cathode potentials respectively

This equation shows that E_r increases with increasing the concentration of caustic alkali. Actually neither hydrogen nor oxygen is evolved at E_r , and an overvoltage is required to produce hydrogen and oxygen at a finite rate. Overvoltages are mainly evaluated as a function of current and temperature. The total overvoltage is a sum of activation or charge transfer overvoltage, η_a , concentration (or diffusion or mass transfer) overvoltage, η_c , and resistance (or ohmic) overvoltage η_r . Hence:

$$\eta_t = \eta_a + \eta_c + \eta_r \quad (2-13b)$$

(i) Activation Overvoltage

The activation energy, required to promote the electrochemical reaction, appears as a voltage increase over E_r . This is known as activation overvoltage, η_a . As an electrochemical reaction rate is given by the current, the following relation (Butler - Volmer equation) is established between η_a and current density⁽⁴⁾:

$$i = i_o \left(\exp(\alpha n F \eta_a / RT) - \exp\{-(1 - \alpha) n F \eta_a / RT\} \right) \quad (2-14)$$

where

i_o = exchange current density (current at $\eta_a = 0$),

α = transfer coefficient (considered as constant),

i_o is in direct proportion to the densities of effective areas and active sites and the activities of electrode reaction substances. It increases exponentially with increasing temperature and decreasing activation energy for the electrode reaction.

(ii) Concentration Overvoltage

Due to mass transfer limitations of negatively charged ions produced at the cathode, the electrode potential will be more negative than E_c at the cathode and more positive than E_a at the anode and the voltage required to electrolyze water is thus larger than $E_a - E_c$. This voltage increase is called concentration overvol-

tage, η_c , which is expressed as⁽⁴⁾

$$\eta_c = \frac{RT}{nF} \ln \left(\frac{i_L}{i_L - i} \right) \quad (2-15)$$

where i_L is the limiting current density. The electrolyte should preferably be stirred or circulated to reduce concentration overvoltage.

(iii) Resistance Overvoltage

The ohmic drop in voltage occurred between the working electrodes is known as resistance overvoltage, η_r . It is expressed as⁽⁴⁾

$$\eta_r = I \cdot R_s \quad (2-16)$$

where R_s is the electrical resistance of the electrodes and the electrolyte materials to used.

Hence, the actual voltage, V_t , required for electrolysis is given by (Figure 2.5) :

$$V_t = V_r + \eta_t \quad (2-17)$$

In case of platinum electrodes, it is found that the minimum voltage which must be applied-before gas bubbles appear-is close to 1.7.

The voltage efficiency, E_v , is expressed by:

$$E_v = V_r / V_t \quad (2-18)$$

2.5.2 Current Efficiency

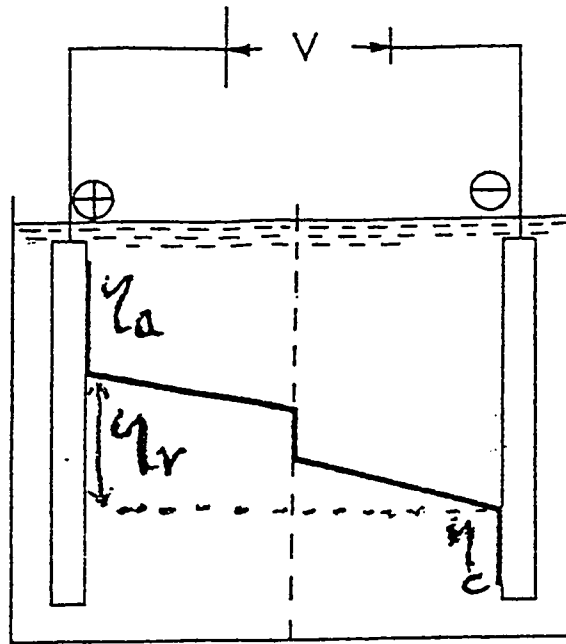


Fig. 2.5 The voltage components in a two compartment electrochemical reactor

In general, the current efficiency of electrolysis, E_i , is given by

$$E_i = \frac{\text{Actual Amount of useful Product}}{\text{Theoretical Amount of Product Equivalent To Electricity Used}} \quad (2-19)$$

In order to make E_i large, it is necessary to reduce the formation of by-products and other side reactions. The value of E_i is generally high in water electrolysis.

2.5.3 Energy efficiency

Energy efficiency of electrolysis, E_g , is given by :

$$E_g = E_v E_i \quad (2-20)$$

The energy consumption U is represented by

$$U = V_t * I * t \quad (2-21)$$

where t is the time of electrolysis.

The amount of production at the electrode, m , is expressed as

$$m = \theta * I * t * E_i \quad (2-22)$$

where θ is the electrochemical equivalent ($\theta = 0.037607$ g /Ah for hydrogen). A highly efficient cell would require 3.245 kWh of electrical energy, for each 1m^3 hydrogen (at S.T.P) of this 3.245 kwh, 2.693 kWh has to be applied as electrical energy and the remainder supplied as heat. For most industrial electrolyzers, 4.2 to 4.9 kwh is required to produce 1 m^3 hydrogen

2.6 INDUSTRIAL WATER ELECTROLYSIS

All research programs in the area of the water electrolysis share two main objectives⁽¹¹⁾:

- (i) To improve energy efficiency, of converting electricity to hydrogen, and
- (ii) To reduce the product cost.

During the last decade, the research objective was to achieve consumption of less than 4.5 kWh m^{-3} . The adopted approach was improvements in water electrolysis, and much lower energy consumption via vapor phase electrolysis using the thermodynamic and kinetic advantages associated with high temperature operations. Justification for continued efforts to develop cost-effective high-temperature electrolyzers was emphasized by trade-off analysis and techno-economic analysis of water vapor electrolysis cells operating at 1000°C and integrated into process design involving electrical and thermal energy derived from coal. Recent estimates of production costs of hydrogen by the newly developed methods are double the steam-reforming costs, half the cost of the conventional water electrolysis and cost-comparable to the coal gasification process⁽²⁴⁾. One of the most important factors in the water electrolysis is to optimize electrocatalysts which are primarily Ni and Co based compositions. While several coatings have been developed exhibiting electrocatalytic activity, an understanding of the kinetics on high surface area composites is lacking and should be examined in detail to be in a position to predict and develop cost-effective catalysts⁽¹¹⁾. Pathways involved in oxygen evolution reaction are more complex than those proposed for the hydrogen evolution reaction^(12,13) since discharge of O_2 occurs on

oxide covered on non-metallic surfaces. In the last decade, a number of mixed transition metal oxide catalysts-especially spinels and perovskites of Ni, Co and/or Fe were examined⁽¹⁴⁻¹⁶⁾. Of these, Ni Co₂O₄ and Li-doped Co₃O₄ appear promising. Oxygen evolution on these oxides appear to involve formation and subsequent decomposition to higher oxide, and good correlation between the redox oxide couple and the minimum potential for O₂ evolution has been established. Never-the-less, oxygen overpotential is still high and identification of pathways, and relationship of the kinetics to the electronic and steric properties requires deep studies to realize an understanding of the proposed interaction of reactants and absorbed intermediates with oxide surfaces.

2.7 SEA WATER ELECTROLYSIS (SWE)

As far as the electrolysis of sea water, as a source of hydrogen, is concerned, two options exist for performance of this electrolysis. The first option is, to subject the water to total desalination to remove all dissolved salts and produce essentially distilled water. This distilled water can then be subjected to electrolysis, in conventional, alkaline-electrolyte electrolysis cells.

The disadvantages of this approach are the additional capital cost of water treatment and desalination system, and the environmental problems arising from the need to dispose the residual salts removed during desalination. The advantages are the ability to use developed technology, for the direct electrolysis of fresh water.

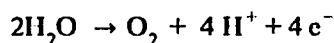
The second option, is to design an electrolyzer system capable of utilizing sea water for direct electrolysis. It is probable that these systems would operate at a low power density and electrolyze only a small portion of the water in contact with electrodes. The disadvantages are many: new technology must be developed to solve the probable corrosion and contamination problems and the evolution of undesirable electrochemical products such as chlorine. The advantages are possible lower capital cost and natural elimination of the waste brine which is only slightly enriched with salts. It may also be possible to recover economically significant quantities of the metals present in sea water that are less active electrochemically than hydrogen such as : silver, gold, mercury, magnesium⁽²²⁾ and copper⁽²⁰⁾ .

Solar collectors utilizing direct solar radiation, ocean thermal gradient and other sources of renewable energy such as wind make sea water, and its direct electrolysis, as the most convenient source of hydrogen on a very large scale. This goes along with the new concept of hydrogen economy^(1,7,23,24) .

2.7.1 Theory of SWE

By applying the Nernst equation to standard electrode potentials it can be seen that oxygen evolution is actually the thermodynamically favoured anodic reaction, occurring significantly less anodic than chlorine in neutral seawater. Such a superficial analysis is highly misleading. However, two major factors are responsible for the evolution of chlorine at practical operating conditions.

First, in unbuffered solutions, such as seawater, both oxygen and chlorine evolution cause the solution adjacent to the surface of the anode to become acidic. This is obvious for the case of oxygen evolution which generates H^+ as follows :



Any chlorine generated at the anode undergoes immediate hydrolysis which also generates H^+ as follows:



As the anode becomes more acidic, the thermodynamic voltage for oxygen evolution becomes more anodic, a trend favoring chlorine evolution which is independent of pH. As power is first applied to an anode, the theoretical voltage for oxygen evolution will therefore become more anodic according to the equation¹⁷

$$E_{O_2} = 1.23 + \frac{RT}{F} \log (a_{H^+}) + \frac{RT}{4F} \log P_{O_2} \quad (2-23)$$

The steady-state pH of the solution adjacent to the anode, and hence the voltage at which the anode operates during continuous electrolysis, is dependent prima-

rily on conditions of flow rate and current density. Bennett⁽¹⁸⁾ showed experimentally that the effective anode pH - under practical conditions of electrolysis - is about pH 1 - pH 2 , and even when the effective anode pH becomes very low, oxygen evolution is thermodynamically preferred to chlorine evolution because equilibrium potentials of oxygen evolution are lower than those of chlorine (see Figure 2.6), by about 200 mV. This analysis is incomplete, however, since thermodynamic voltages are valid only at zero current flow. The second factor which then inhibits the evolution of oxygen is its well-known high overpotential at practical current densities. The difficulty of evolving oxygen relative to chlorine is illustrated by a comparison of their exchange current densities which is an indicator of the ability of an electrode to catalyze a given electrochemical reaction. The ratio of exchange current densities for chlorine and oxygen evolution on most anode materials is very high⁽¹⁸⁾

$$\frac{i_{o_{Cl_2}}}{i_{o_{O_2}}} = 1 \cdot 10^3 - 1 \cdot 10^7 \quad (2-24)$$

which is a measure of the ease of evolving chlorine relative to oxygen .

The voltage range for the decomposition of a H₂-Cl₂ cell is between 1.8 - 2.2 V depending on current density. The H₂-Cl₂ cell begins to function at a higher applied potential difference than the H₂-O₂ cell. The evolution of Cl₂ will replace O₂ evolution between 1.8 - 2.2 V⁽¹⁾ . However, the transport of ions to the electrode is limited, whereas there is no corresponding problem with the

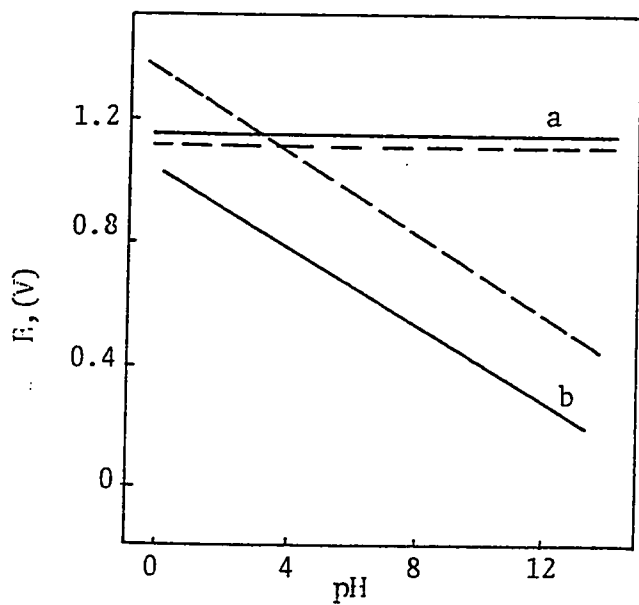


Fig. 2.6 Potential - pH diagram⁽²⁵⁾
 (a) chlorine (b) oxygen reaction
 — thermodynamic equilibrium conditions
 --- kinetic conditions for electrolysis

availability of water. Hence, there will be a potential sufficiently high at which there will be no increase in evolution rate of Cl_2 , whereas that of O_2 will increase with potential as shown in figure 2.7. A precise calculation of the transport control of chlorine ions will depend (as with the pH at the interface) upon a knowledge of the transport conditions, e.g. natural and forced convection⁽²¹⁾. Therefore, electrolysis of seawater at low current density, $< 1\text{mA}/\text{cm}^2$, will result in exclusive evolution of oxygen, while operation far in excess of the limiting current for chloride oxidation will favour oxygen evolution. Limiting current in practical cells ranges from⁽¹⁸⁾ $100 - 1000\text{ mA}/\text{cm}^2$, however, an operation at several thousand cm^2 would be necessary to achieve high coulombic oxygen efficiency. This is also considered impractical since I.R. heating and power consumption would become unreasonably high at such current densities.

The only major cathodic reaction in seawater is hydrogen evolution. Although hydrogen evolution occurs at high coulombic efficiency, it also causes a localized pH change, resulting in a higher cell voltage and causing deposit formation. As the cathode surface becomes more basic during electrolysis, the thermodynamic voltage for hydrogen evolution becomes more cathodic according to the equation⁽¹⁷⁾

$$E_{\text{H}_2} = \frac{RT}{F} \log (a_{\text{H}^+})_{\text{cat}} - \frac{RT}{2F} \log P_{\text{H}_2} \quad (2-25)$$

As with the anode reaction, the actual pH of the solution adjacent to the cathode, and hence the voltage at which the electrode operates during electroly-

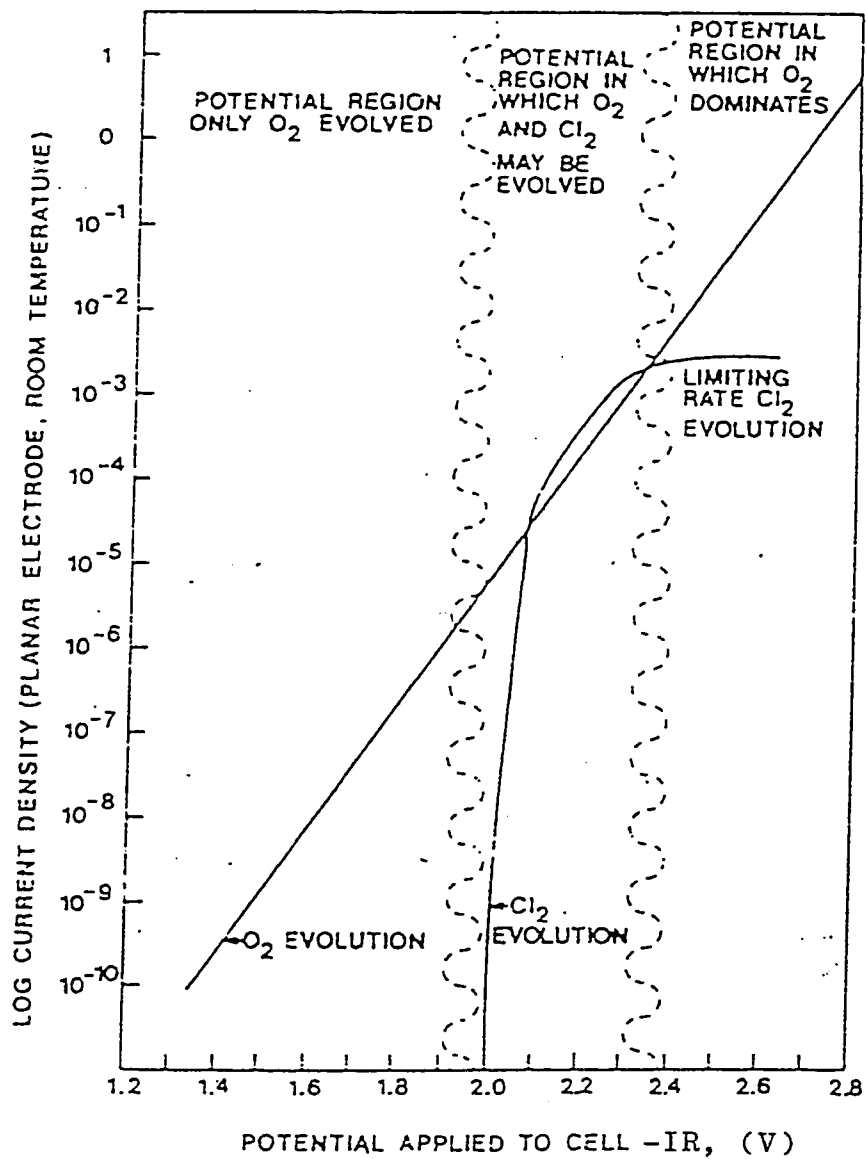


Fig. 2.7: Chlorine and Oxygen evolution in sea water electrolysis⁽¹⁾.

sis, is dependent on conditions of flow rate, current density, and temperature. Effective cathode pH usually ranges from pH 11 - pH 14.

The basic nature of the solution at the cathode surface results in a surface deposit which is the most troublesome operational problem encountered with the electrolysis of seawater (see figure 2.8). A chemical precipitation of magnesium hydroxide occurs at a pH > 9, and specifically, at 10.7 - 11.0 as reported by Kirk⁽¹⁹⁾ and Bennett^(18,30) respectively. Williams⁽²⁰⁾ has carried out direct electrolysis of sea water, using carbon electrodes, and he reported the precipitation of calcium hydroxide . Magnesium hydroxide adhesion and later growth onto neutral surfaces of nickel cathode , was reported by Kirk⁽¹⁹⁾ . Magnesium Hydroxide causes even higher pH at the cathode interface and will eventually clog the electrode gap. Such deposits cannot be eliminated entirely, but they can be effectively minimized by high seawater turbulence and proper choice of current density and cathode surface.

2.7.2 Problems of SWE

The effectiveness of utilizing direct solar radiation, ocean thermal gradients and other sources of renewable energy in producing hydrogen depends primarily upon solving the problems of SWE.

Ecological requirements, the absence of sufficient chlorine evolution at SWE, make it necessary to work out ways either of its utilization, or changing the $H_2 - Cl_2$ cell for $H_2 - O_2$ one.

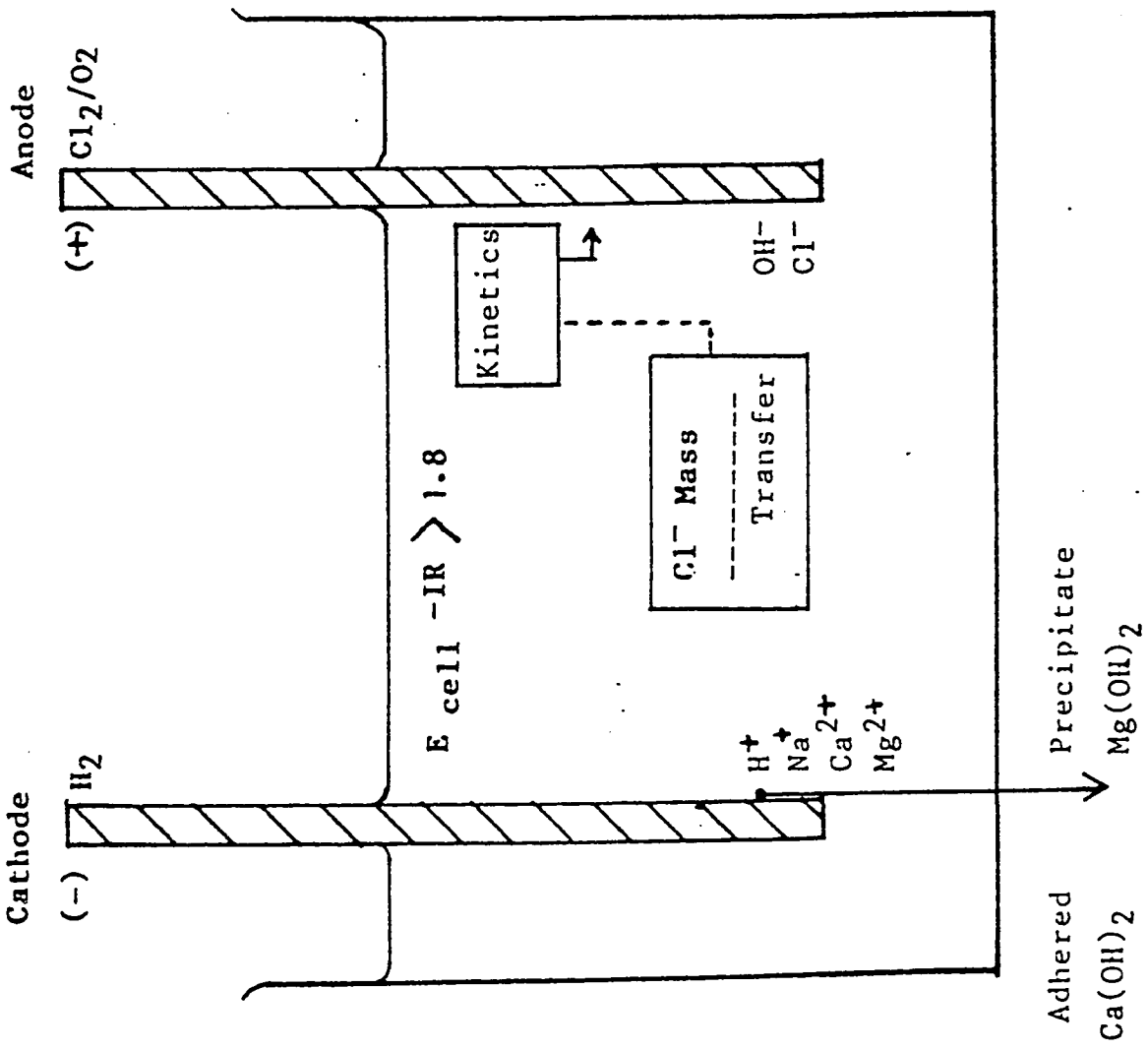


Fig. 2.8 Schematic diagram illustrating the electrolysis process

Different ways of solving these problems were suggested. Bockris⁽¹⁾ considers the possibilities of SWE at a depth of about 1 km with hydrogen evolution at about 100 atm and its storage at a depth with simultaneous interaction of chlorine with alkali and its subsequent release to sea and reaction with water at the surface platform at 650°C. This, however, raises appreciably the total hydrogen cost.

2.7.3 Selectivity of oxygen evolution reaction at SWE

The most promising way for evolution of oxygen rather than chlorine at the anode is creating anodes selective in the conditions of electrolysis of diluted chloride solutions to oxygen evolution on the basis of using electrocatalytic approach, connected with modification of electrode surface. Such electrode may be created by modification of well-studied oxide rutenic titanic anodes and other types of DSA with special manganese dioxide^(26,27).

Oxygen reaction depends rather upon the electrode material, than chlorine reaction does at low overpotential with different electrode materials. Kinetic conditions of the reaction, may lead to the changes of curve position from those shown in Figure (2.6). Thus, in the interval of a pH between 0 - 3, chlorine evolution reaction potential is lower than oxygen evolution reaction potential. Relative curve positions of these two reactions also depend upon the densities of polarizing current, as the speed of overvoltage increase is different for oxygen and chlorine evolution reactions.

As the industrial electrolysis is conducted at high current densities the relative values of the two exchange current densities, $I_{\text{oCl}_2} = 1.3 \cdot 10^{-3}$ and $I_{\text{oO}_2} = 6 \cdot 10^{-10}$ A/cm², are likely to be less important than relative values of the Tafel slopes.

On the whole, the selectivity of chlorine depends on the electrolyte composition and concentration, the temperature, current density, and the electrode material. At high current densities partial speed of oxygen evolution is less dependent on electrode material of composition. Most works on selectivity of chlorine and oxygen reactions are based on the simplicity of controlling the selectivity of chlorine reaction with the help of kinetic factors, than that of oxygen reaction.

As mentioned above, oxygen evolution should predominate under the conditions of pH of sea water and in diluted chloride solution (See Figure 2.6). Local acidifying of a near-anode layer and kinetic conditions lead to predominance of chlorine in a wide range of current densities⁽²⁸⁾. Oxygen evolution at high speed on electrode systems with MnO₂ covering was pointed out to be possible⁽²⁵⁾.

2.7.4 SWE and Corrosion

To solve problems related to electrolysis of diluted chloride solutions, it is not only necessary to obtain high electrocatalytic activity and selectivity of electrode materials, but also to study their corrosive behavior. Kondrikov⁽²⁹⁾ discov-

ered the great decrease of the corrosive stability of oxide anodes on titanitic base in diluted chloride solutions at low temperature (about 0 °C). It was determined that the period of current decrease to the half of its value from the initial value, for systems analyzed by Kondrikov at the above conditions, is within the limits from several to dozens of hours depending on pH of diluted chloride solutions and the nature of oxide covering of anodes.

From the above survey, it is obvious that SWE is not fully developed both in theoretical and technological aspects⁽²⁵⁾ compared to alkaline water electrolysis. The effect of different salinity (NaCl concentration), cell overvoltage, current density levels on hydrogen production rate and efficiency of hydrogen produced in SWE are important for any future study of the seawater hydrogen economy.

CHAPTER THREE
EXPERIMENTAL

CHAPTER THREE

EXPERIMENTAL

In this chapter, the apparatus, and materials used, and the experimental technique are described. The chapter is divided into six sections:

3.1 The Apparatus.

3.2 Experimental Technique.

3.3 Assessment of Chlorine content.

3.4 Cathode Precipitate Analysis.

3.5 Assessment of The Decomposition Voltage.

3.6 Application of Solar Energy.

The total number of experiments carried out were 109 taking 4 - 10 hours per run. The parameters investigated and their ranges and levels are given in Table 3.1.

3.1 THE APPARATUS

The apparatus is composed of:

- 1) Hoffman electrolysis cell.
- 2) Power supply
- 3) Solar panel

Table 3.1 Experimental design.

Parameter	Description	No. of Levels
Salinity	Eight solutions of 14 %- 200% sea water concentration and one solution of natural sea water	9
Voltage	6 - 20 V	6
Current Density	25 - 126 mA/cm	6
Quantity of Electricity	500 - 1500 C	3

and the following equipments and instruments were used :

- 1) Atomic Absorption (AA)
- 2) Ion Coupled Plasma (ICP)-Atomic Emission Spectroscopy (AES)
- 3) Ion chromatography
- 4) Mercury Dropping Electrode (MDE)
- 5) Digital voltmeter
- 6) Digital ammeter
- 7) pH meter (Fisher Model 805)
- 8) Resistances

3.2 EXPERIMENTAL TECHNIQUE

Electrolysis of synthetic sea water, prepared in the laboratory, and natural sea water (from EL-Khobar beach on the Arabian Gulf) was carried out in a 200 ml electrolysis apparatus which uses the basic Hoffman arrangement as shown in Figure (3.1a). The cell has two vertical graduated gas collecting tubes with stopcocks at the top, joined by a bridge tube at the bottom which is connected to a reservoir. The apparatus was manufactured by Sargent-Welch Scientific Co. (S-29125). One of the glass stopcocks was changed by teflon to avoid the escape of chlorine received at the anode. Gases produced at the cathode and the anode were collected by the displacement of saline water. Platinum planar electrodes (1.90 cm * 0.40 cm * 0.01 cm thickness) were used and held in the lower ends of the gas collecting tubes by means of rubber stoppers which fit closely into the tapered lower ends of the tubes. Each collecting tube was graduated downward from the 0 to 60 ml in increment of 0.2 ml.

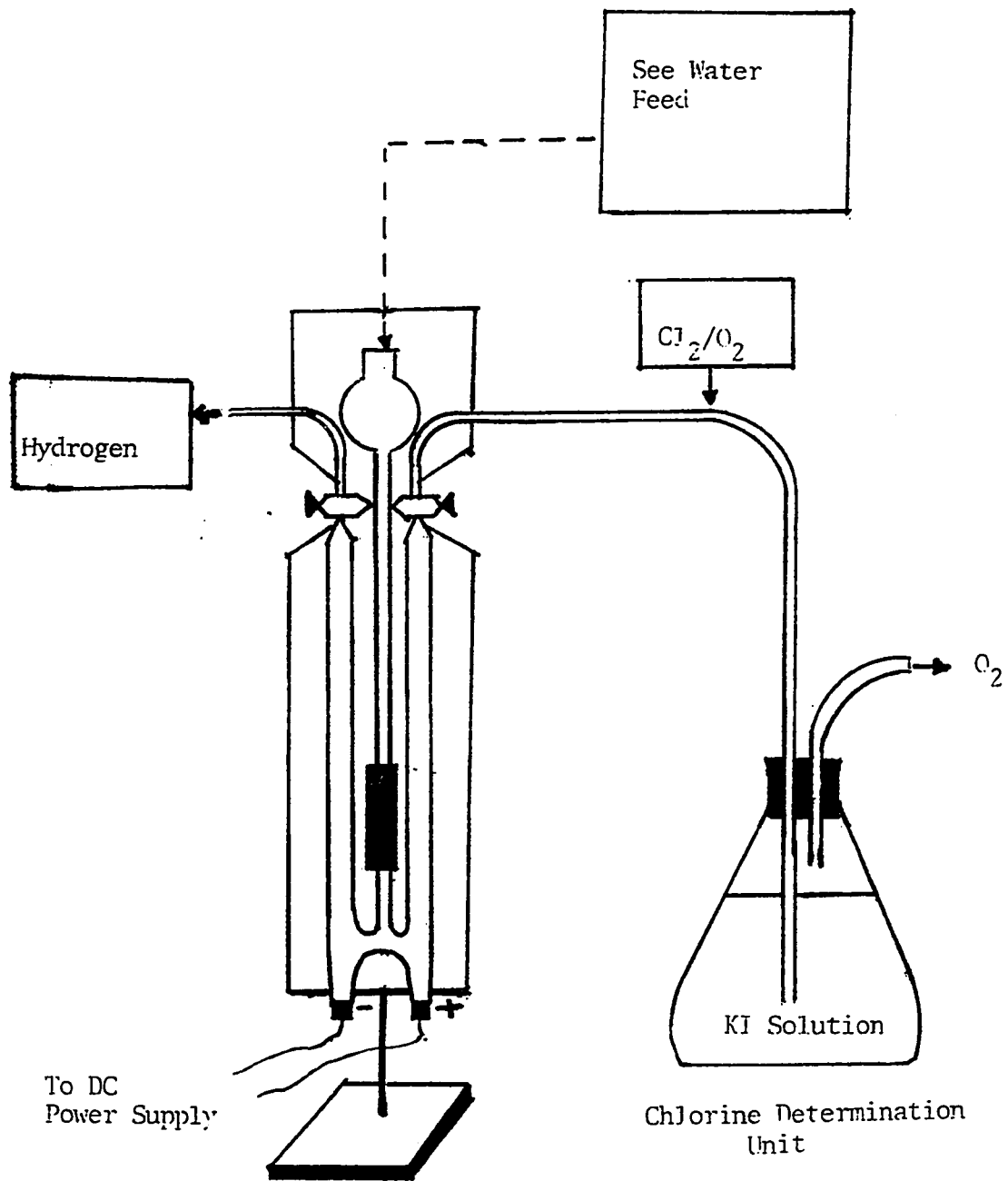


Figure 3.1a Experimental set-up.

The energy input to the cell is a DC current obtained from a power supply which is connected to an AC source. The power supply is a Farnell type (Model LT 30-2) and could be operated as a potentiostat by shifting to the Constant Voltage (CV) mode and connecting the electrolysis cell directly to the power supply, or as a galvanostat by shifting to the Constant Current (CI) mode and connecting a resistance R_s calculated from

$$R_s = \frac{1}{IL_{\max}}$$

where IL_{\max} is the maximum load current. See Figure (3.1b).

The solutions used were prepared using deionized water. Sea water was simulated (Synthetic Sea Water) by NaCl and $MgCl_2$. Solutions 1 - 4 contain NaCl only and 5 - 8 ($NaCl + MgCl_2$), (Table 3.2). The concentrations of the synthetic sea water (5 to 8) are referred to in the text by the Total Dissolved Solids (TDS) of 62.70, 31.35, 15.67, and 4.48 g/L and represent 2,1,0.5,0.14 times the concentration of synthetic sea water (solution 6). This simulated composition of sea water was chosen to cover the range from desalination rejects to brackish water. Natural sea water was analysed for cations and anions. Cations were determined by ICP-AES, Gold and Silver by AA, and anions by Ion Chromatography. The results are given in Table 3.3. The pH of the natural sea water was reduced to 6.1 by addition of HCl.

Solutions 1-8 and natural sea water were electrolyzed under potentiostat and galvanostat conditions in the range of 6-20 V and 25.3-126.3 mA/ cm^2 up to

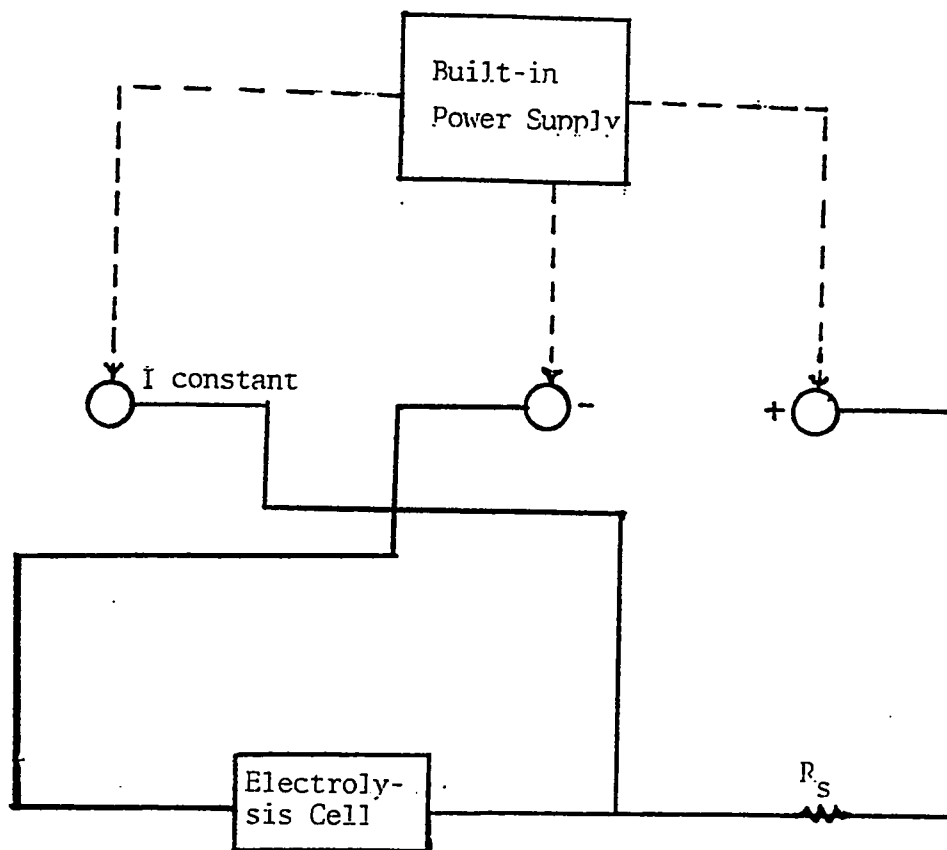


Figure 3.1b Circuit diagram for galvanostat mode (constant I)

Table 3.2 Composition of solutions used in this research

Electrolyte	Concentration (mol/L)							
	1	2	3	4	5	6	7	8
Na⁺	0.9040	0.4520	0.2260	0.0646	0.9040	0.452	0.2260	0.0646
Mg²⁺	-	-	-	-	0.1046	0.523	0.0262	0.0075
Cl⁻	0.9040	0.4520	0.2260	0.0646	1.1132	0.5566	0.2783	0.0796
Total (mol/L)	1.8080	0.9040	0.4520	0.1292	2.1218	1.0609	0.5305	0.1517
concentration (g/L)	52.830	26.42	13.21	3.78	62.70	31.35	15.67	4.48

Table 3.3 Composition of natural sea water

Element	Concentration (mg/L)
Na	14240
Mg	1607
Cl	26360
Ca	548.1
K	518.2
SO	3658
Al	0.85
Ag	< 0.02
Au	< 0.02
Hg	< 0.05
Br	99.3
F	< 1.0
I	0.05
TOTAL	34217

1000 C of electricity as well as 500 C and 1500 C for natural sea water. The volumes of hydrogen produced at the cathode and other gases at the anode as well as the variation in current for constant voltage and variation in voltage for constant current were obtained.

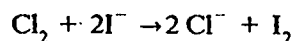
3.3 ASSESMENT OF CHLORINE CONTENT

Chlorine is a major anode-gas product in the electrolysis of saline water containing chlorides. In this research iodometry and ascorbinometric titrations are coupled for the analysis of chlorine.

L-Ascorbic Acid was used for the determination of chlorine in gas phase, chlorine, hypochlorite, and chlorite in the liquid phase. The acid was dried under vacuum at 50° C⁽³¹⁾ and the 0.1 N solution was prepared using deionized water and stored near 0°C after addition of 4 ml of formic Acid and 0.1 g of Na₂EDTA per litre to retard atmospheric oxidation⁽³²⁾. The acid was standardized against 0.1 N standard iodine solution. Erdey⁽³²⁾ showed that the error of the determination of 15-150 mg chlorine is less than +0.5%.

For the determination of chlorine in the gas phase the following procedure was followed :

(i) The anode-gas was passed through a 50 g/L KI solution where chlorine will react immediately and an equivalent amount of iodine is liberated as follows :



(ii) Titration with Ascorbic Acid (.01 N) follows immediately and ascorbic acid reacts smoothly and instantaneously with iodine, leading to the formation of dehydroascorbic acid, iodide ions, hydrogen ions being liberated:

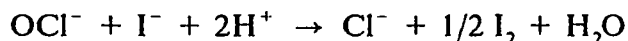


The media is always acidic and the end point for the oxidation/reduction reaction between ascorbic acid and iodine is visually detected on a white background by the disappearance of the iodine color (more precisely, of triiodine ions), clearly (1ml of acid = 0.3545 mg Cl).

For the determination of chlorine, hypochlorite and chlorite (available chlorine) in the liquid phase the following procedure⁽³²⁾ was followed.

- (i) 5 g of KI were added to liquid phase after electrolysis.
- (ii) The pH of the solution was recorded.
- (iii) 15 ml of 10% H₂SO₄ was added to a 50 ml of this solution.
- (iv) After 10 minutes the solution was titrated with, 0.01 N Ascorbic Acid.

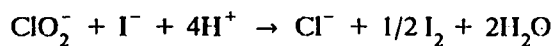
Hypochlorites react with KI in an acidic medium as follows:



Iodine can then be titrated with ascorbic acid .

The Acid should always be added after the addition of KI.

The chlorites react as follows:



This reaction is slow and the time span after the addition of H_2SO_4 is for the completion of the chlorite reaction.

1 ml of 0.1 N ascorbic acid is equivalent to 3.545 mg of chlorine (Cl) available in the form of free chlorine, hypochlorite or chlorite.

3.4 CATHODE PRECIPITATE ANALYSIS

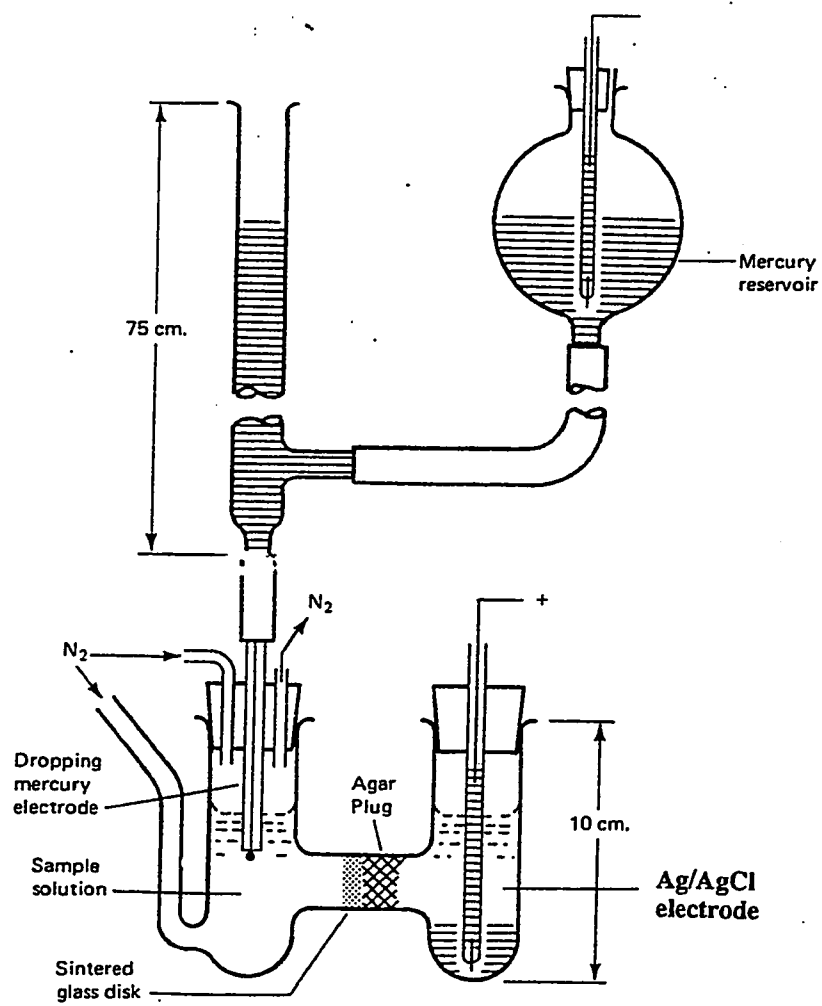
At the end of each experiment run the cathode was dried, and the precipitate was dissolved in a 10 ml of 1 M HCl, and precipitates from solutions 5-8 and natural sea water were analyzed by AA. for Mg and Ca .

3.5 ASSESMENT OF THE DECOMPOSITION VOLTAGE

The determination of the decomposition voltage of saline water was carried through polarography. Polarography is a class of voltammetry in which the working electrode is a dropping mercury electrode (DME) . A typical polarographic cell is shown in Figure 3.2 . The reference electrode is Ag/AgCl electrode (standard electrode potential is 0.2224V) .

In principle, any microelectrode could be used for the working electrode, but the DME has a number of disadvantages over the others :

- 1) Mercury has a high hydrogen overpotential .
- 2) The surface is continually renewable and so it does not become contaminated or changed by the deposited metal .
- 3) The surface area is also renewable .



F.g. 3.2 Polarographic cell

Polarograms for solutions 1-8 and natural sea water were obtained in a mercury dropping electrode Analyzer (type EG&G- PAR model 384 B SMDE DC mode) after calibration with a standard 2.5 ppm Cd^{2+} in buffer acetate with 4.5 pH value. Ag/AgCl was used as a reference electrode. The following procedure was followed in obtaining the polarograms:

- (i) Initial pH values of samples were obtained.
- (ii) Ten ml of each sample was deaerated for 240 seconds with N_2 gas at room temperature (22°C).
- (iii) Simultaneous runs of the DME were made.
- (iv) Automatic potential scanning at 200 mV/min and 10 minutes were required to obtain the polarogram, exclusive of the time for deaeration.

3.6 APPLICATION OF SOLAR ENERGY

Natural sea water was then electrolyzed using solar energy using a solar photovoltaic panel manufactured by Solec Inc. (Model S-4319) with an effective surface area of 0.439 m^2 . These tests were performed during the second half of Nov. 1991. Solar output and hydrogen production rates were recorded on hourly basis. The circuit diagram is as shown in Figure (3.3), where R is a resistance

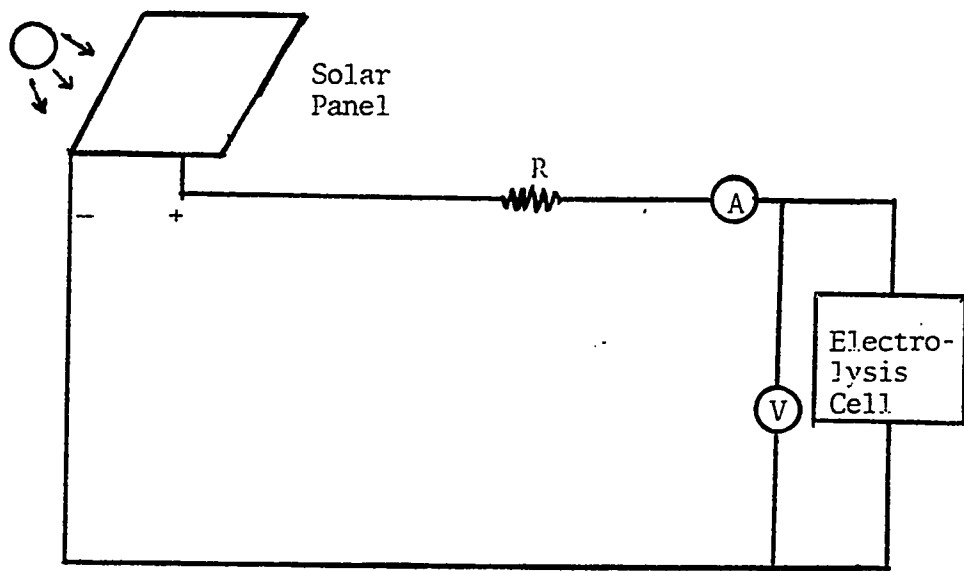


Fig. 3.3 Circuit diagram for solar energy source.

CHAPTER FOUR
RESULTS AND DISCUSSIONS

CHAPTER FOUR

RESULTS AND DISCUSSIONS

In this chapter the most important experimental findings are reported and discussed. This includes hydrogen production, chlorine in gas and liquid phase, hydrogen to chlorine ratio, and magnesium adhered precipitate.

4.1 HYDROGEN PRODUCTION

Hydrogen production rate for NaCl solutions as well as synthetic and natural seawaters was measured at different current densities and voltages.

For the solutions investigated, it was found that the hydrogen production rate was dependent upon the applied current density alone. As can be seen from figure 4.1, the hydrogen produced on a platinum electrode of 1.5835 cm² area is 85 (mL/hr)/ for 120 mA/ cm² change in current density. By Eqn. 2-22 an efficiency of 99% is obtained for this electrolysis process. Other calculations are given in Appendix-A . From figure 4.1 the hydrogen production rate, HPR, in mL/hr and current density, i , in mA/ cm² are related by the equation :

$$\text{HPR} = -0.20832 + 0.7236 i$$

The same conclusion is reached from figure 4.2, which is a plot for the hydrogen production rate versus the total dissolved solid (TDS) at different current densities.

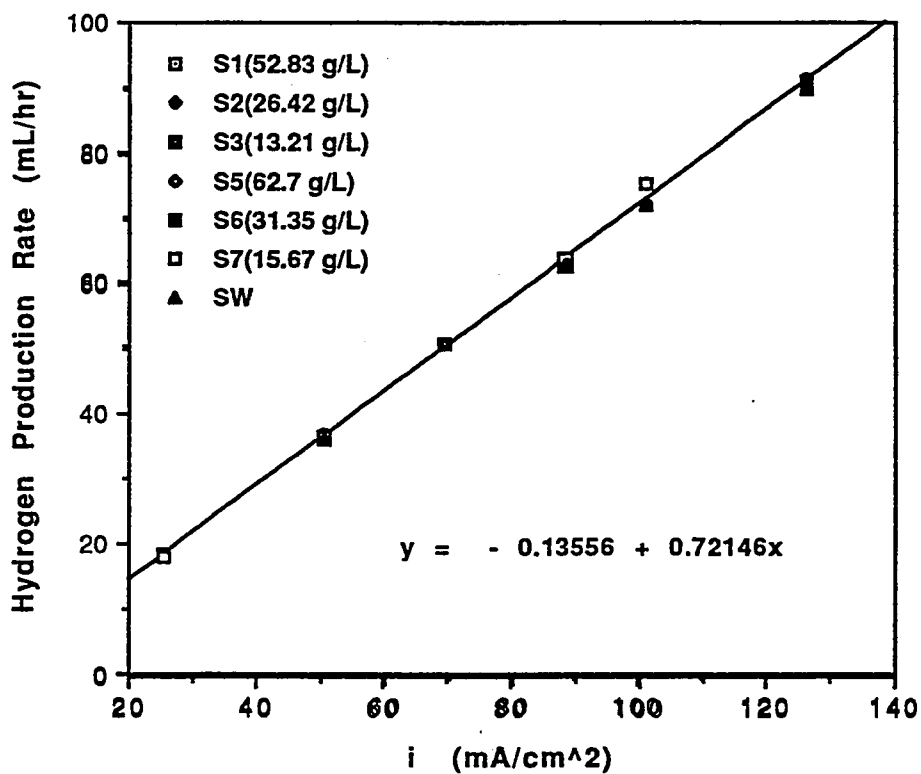


Figure 4.1 Hydrogen production rate vs. current density for all solutions studied in this research

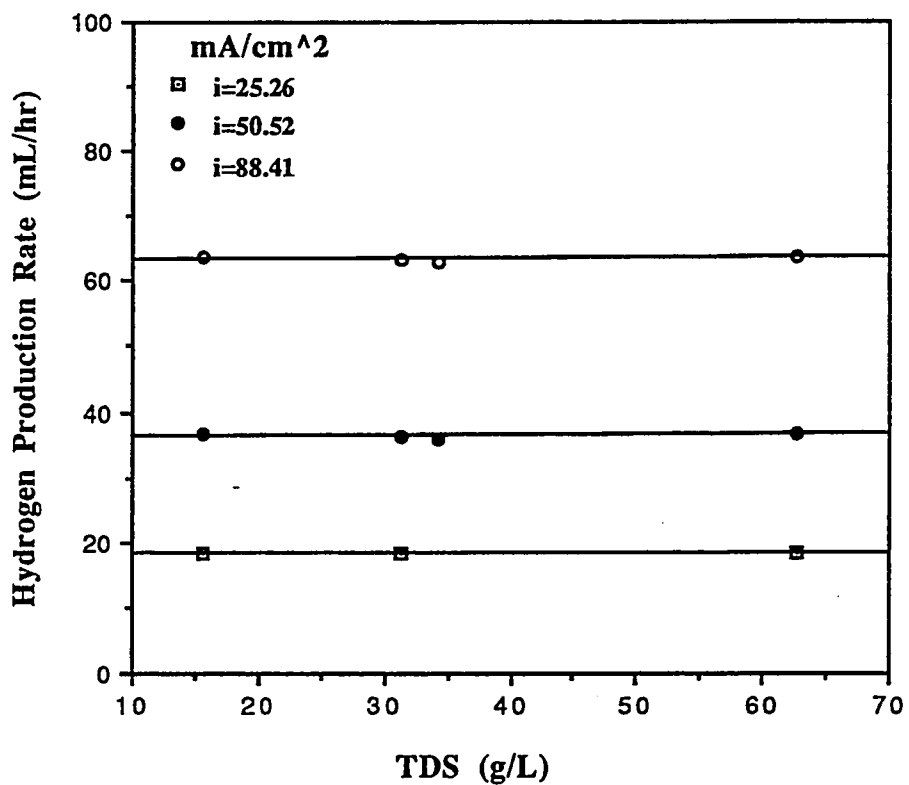


Figure 4.2 Hydrogen production rate vs. TDS for synthetic sea water at different current densities

On the other hand, figure 4.3 shows the relationship between hydrogen production rate and TDS for different voltages applied. Over the range of voltages used in these experiments (6 - 20 V), the hydrogen production increases with the increase in TDS. This is attributed to the increase in conductivity of the salts. On the other hand, this rate, increases ohmically (follows ohm's law) with the increase in voltage for natural and synthetic sea waters. However, the rate of increase at low values of voltage, say 6 - 8 V, is rather slow, since the production rate is dependent on the current density. At higher voltages, (10 V and above), the initial conductivity is no longer affecting the current density and the solution behaves like a resistance with lower resistance at high TDS, hence the increase in salinity level gives a proportional increase in the hydrogen productivity. Hydrogen Production Rate (HPR) and TDS are correlated in the form

$$\text{HPR} = a + b \text{ TDS}$$

Values of a and b are given, for different voltages, in Table 4.1.

4.2 CHLORINE EVOLUTION

Chlorine is a major anode-gas product in the electrolysis of saline water containing chlorides. The first work done by Williams⁽²⁰⁾ on the direct electrolysis of sea water reported the use of a GC in analyzing the chlorine content of the anode-gas. Inaccuracies resulting from the use of the GC in chlorine analysis arise from the fact that chlorine is heavier than oxygen and tends to be at the bottom of the gas phase which makes the homogeneity of the sample taken for analysis very weak. This is added to the usual difficulties associated with gas

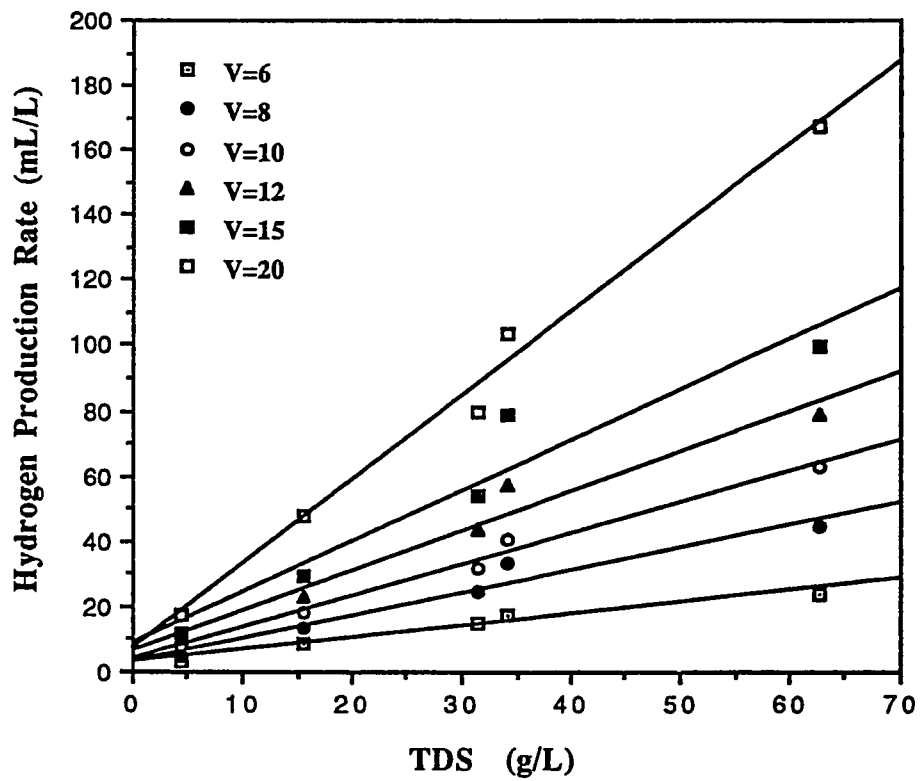


Figure 4.3 Hydrogen production rate vs. TDS for sea waters at different voltages

Table 4.1 Correlation of hydrogen production and TDS
 $HPR = a + b \text{ TDS}$

Voltage, V	a	b	Regression coefficient R
6	3.1266	0.35921	0.964
8	3.4531	0.69669	0.952
10	3.8251	0.95703	0.986
12	6.6669	1.2102	0.962
15	8.4566	1.5582	0.924
20	7.0285	2.5703	0.989

sampling. Bennet⁽¹⁸⁾ reported the use of iodometry followed by titrations with thiosulfate. The end point detection using starch is one of the difficulties. Reproducibility of chlorine evolved is within 7%.

4.2.1 CHLORINE IN GAS PHASE

a) Effect of Current Density

Figure 4.4 shows results of natural sea water electrolysis. Chlorine is evolved in the gas phase at different current densities and for different quantities of electricity namely 500 C, 1000 C, and 1500 C.

For 500 C the anode product gas is almost chlorine free regardless of the current density (38-126 mA/cm²). This is mainly due to the absorption of chlorine evolved in the liquid phase. At intermediate values of electricity passed (1000 C), the behavior is almost the same and about 0.25 mmol chlorine was produced in the cell. This is attributed to the enrichment of the anolyte with chlorine evolved, especially in a poor mixing cell. At higher quantities of electricity, the performance of the cell changes to be a current-density-dependent, with the following main features :

At low current densities (< 60 mA/cm²) chlorine evolved at 1500 C is 1.25 mmol which is approximately 5 times that of 1000 C while a factor of 1.5 is expected if it is proportional to quantity of electricity. This is mainly due to the fact that the anolyte is approaching saturation, if not saturated with chlorine. Further increase in the current density decreases the amount evolved in the gas phase significantly because of the enhancement in the absorption rate of chlo-

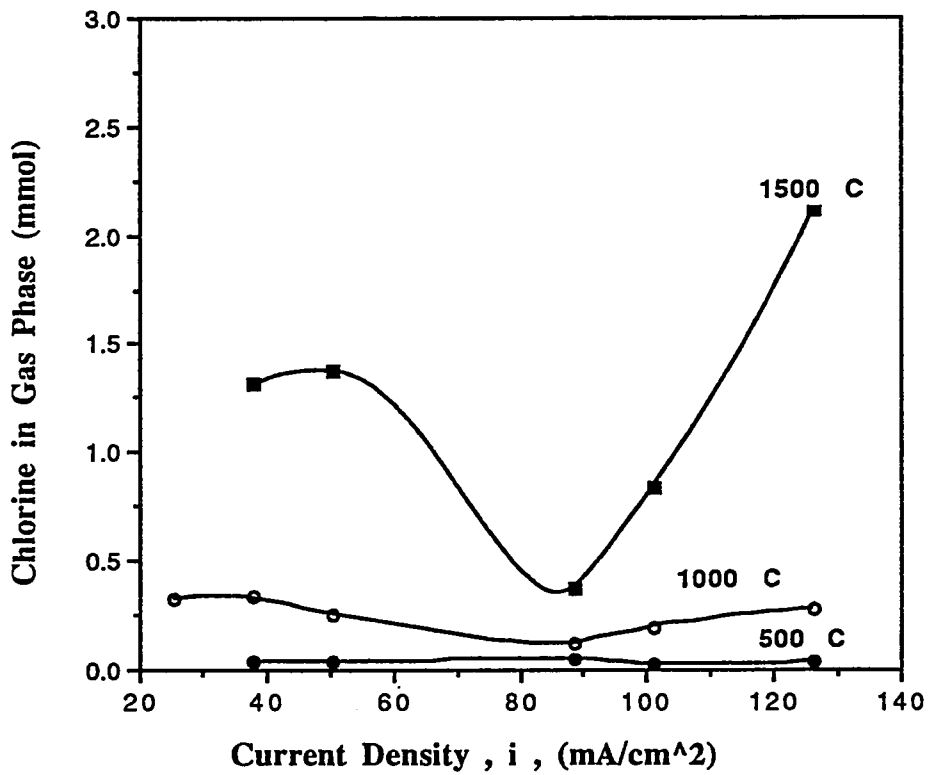


Figure 4.4 Chlorine in gas phase vs. current density for sea water for different coulombs of electricity

rine in liquid phase due to the increase in chlorine evolution rate. Once again, the saturation of liquid phase allows chlorine to appear in the gas phase and higher current densities ($> 100 \text{ mA/cm}^2$) will give higher amount of chlorine in the gas phase.

From the above discussion we conclude that chlorine evolution in the gas phase depends on both current density as well as quantity of electricity. Williams⁽²⁰⁾ reported an increase of chlorine in gas phase with the increase in voltage (i.e. increased current density) but nothing was mentioned about the time duration of the electrolysis, and electrolysis continues till certain volume of gas, enough for analysis, is produced. Accordingly, he concluded that chlorine quantities increase with the increase in current density. Present result show that this is subject to whether time duration electrolysis is enough for the liquid phase to approach saturation for that cell design. Cells with almost chlorine-free anode-gas for sea water electrolysis are possible depending on quantity of electricity and cell design.

Similar results were obtained for NaCl and were shown in Appendix-B.

b) Effect of Chloride Concentration

Figure 4.5 shows the chlorine evolved in the gas phase for different levels of chloride concentration (79.6 - 1113 mmol/L) at different voltages (6-20 V).

For chloride concentration of < 600 (mmol/L) chlorine gas quantities are independent of concentration, but dependent on voltage with higher evolution

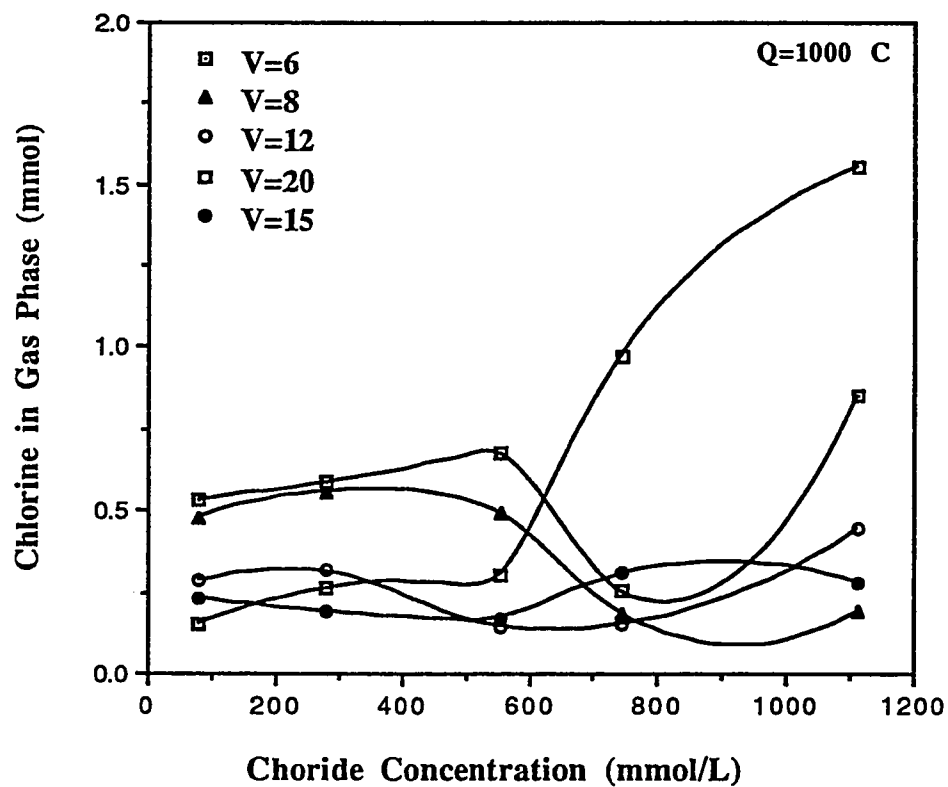


Figure 4.5 Chlorine in gas phase vs. chloride concentration for synthetic and natural sea waters at different voltages

experienced at low voltages i.e. low current densities. However, increased voltage resulted in a lower chlorine evolution in gas phase.

For chloride concentration > 600 (mmol/L) chlorine evolved is absorbed in the liquid phase and low voltages (6 & 8) resulted in a drop of approximately 50% due to the increase in chloride level, while at other voltages it fluctuates.

At 6 V and high concentrations (1113 mmol/L) of chloride the current density (33 mA/cm^2) is low to enhance chlorine absorption in the liquid phase while that of 8V (62 mA/cm^2) resulted in suppression of chlorine in liquid phase. The extreme case of 20 V resulted in a significant increase in chlorine in gas phase for the whole range of $\text{Cl}^- > 600$ (mmol/L) and this is a direct result of high rates of chlorine evolution and saturation in liquid phase.

4.2.2 TOTAL CHLORINE EVOLVED

Total chlorine evolved due to the passage of 1000 C of electricity is determined by adding the chlorine in the gas phase to the "available chlorine" in the liquid phase. The term "available chlorine" includes all free chlorine, hypochlorite, and chlorite. The determination of either Chlorine in gas phase or available chlorine was achieved by the use of ascorbic acid.

a) Effect of Current Density on Total Chlorine from Sea Water

The effects of quantity of electricity as well as current density on chlorine evolved during sea water electrolysis are shown in figure 4.6. It shows that the

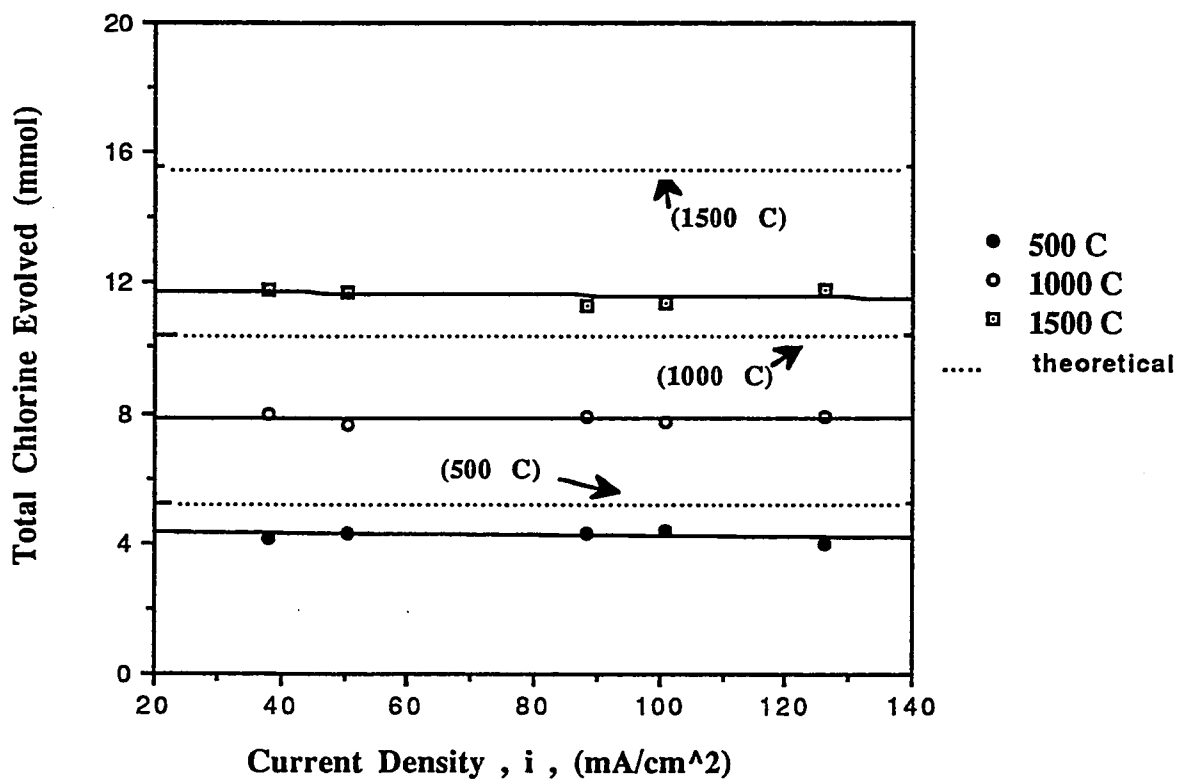


Figure 4.6 Total chlorine evolved vs. current density for sea water for different coulombs

amount of chlorine evolved is proportional to the quantity of electricity applied and independent of current density for the range of current density and coulombs used in this experiment. Dotted Lines represent the theoretical amounts of chlorine evolved as if the current passed is used totally for the production of chlorine alone (i.e. assuming $H_2 - Cl_2$ cell). The difference between the theoretical and the experimental corresponds to the oxygen evolved. Figure 4.7 shows that chlorine evolution is independent of current density, and total chlorine Cl_T , in mmol, is related to quantity of electricity Q , in coulombs by the relation :

$$Cl_T = 0.51913 + 7.37913 \cdot 10^{-3} Q$$

for the range 37.89 - 26.3 mA/cm². Figure 4.8a shows that total chlorine production is independent of current density as well as the chloride level for $Cl^- > 600$ (mmol/L). It is a function of the quantity of electricity passed.

b) Effect of Voltage on Total Chlorine from Sea Waters

Four different concentrations of synthetic sea water (NaCl + MgCl₂) in addition to natural sea water ($Cl^- = 743.52$ mmol/L) are presented by their chloride concentration in figure 4.8b. The total amounts of chlorine produced at different voltages (6-15 V) are shown in the figure. In all cases a quantity of electricity of 1000 C was passed. The total amount of chlorine Cl_T and chloride concentration C (in mmol/L) are related by the equation

$$Cl_T = -3.0918 + 3.8090 \log C$$

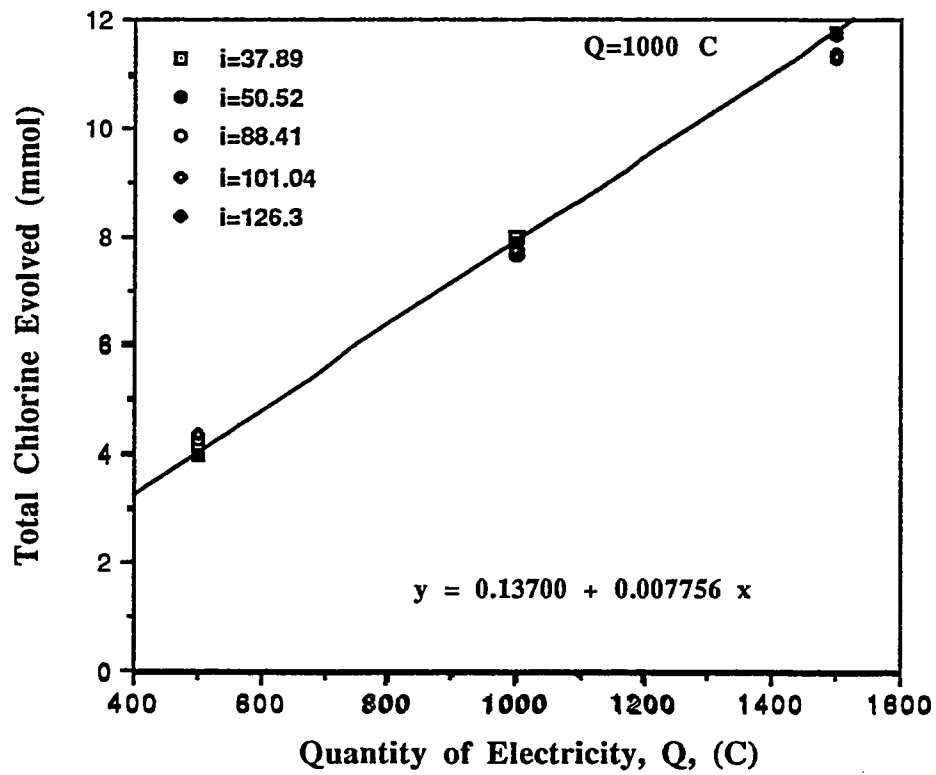


Figure 4.7 Total chlorine evolved vs. quantity of electricity for sea water at different current densities

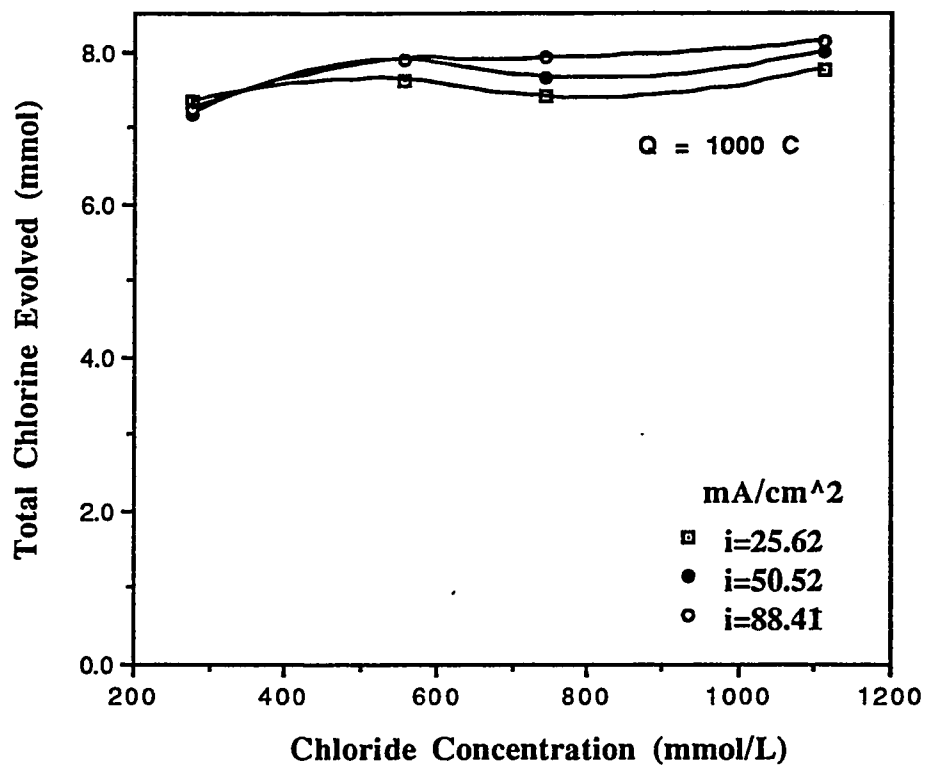


Figure 4.8a Total chlorine evolved vs. chloride concentration for synthetic and natural sea waters

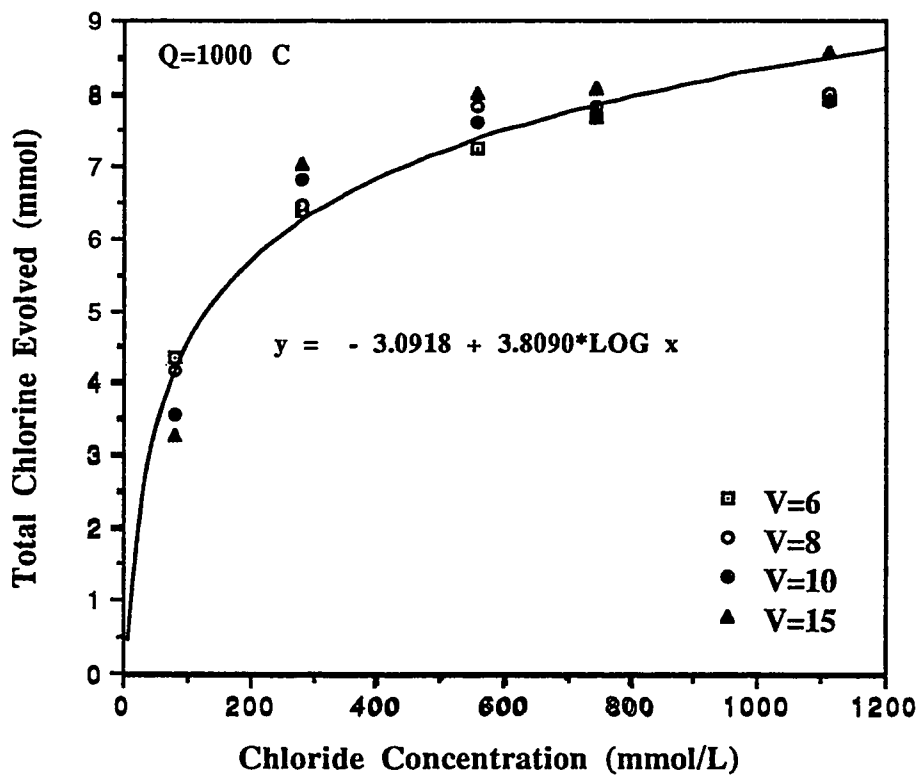


Figure 4.8b Total chlorine evolved vs. chloride concentration for synthetic and natural sea waters

At low chloride levels (< 600 mmol/L) the amount of total chlorine evolved is low in the range of (6-15 V), but it increases with the increase in the chloride content of the solution. This is explained as follows: at low chloride levels the increase in chloride concentration results in a direct increase in solution conductivity as shown in figure 4.9 ($\text{Cond.} = 1.4235 + 8.3304 \log \text{TDS}$). This results in an increased current density for operation at the same voltage. At high chloride concentrations (> 600 mmol/L), the effect on conductivity is insignificant and total chlorine evolved is more or less the same, independent of the chloride concentrations, except for the case of 15 V which shows an increase as compared to other voltages applied.

4.3 HYDROGEN TO CHLORINE RATIO

The total volume of hydrogen produced was measured experimentally and the number of moles of hydrogen was calculated by:

$$PV = ZnRT$$

where Z, the compressibility factor for hydrogen taken equal to unity at 23° C and 1 atm.

The number of moles of chlorine in gas phase or total chlorine on the other hand, was calculated using titration with ascorbic acid as described in chapter 3. It was shown in section 4.1 that, the amount of hydrogen produced is independent of the current density or the voltage for a certain quantity of electricity applied. The ratio of hydrogen to chlorine in gas phase (R1) for 1000 C of elec-

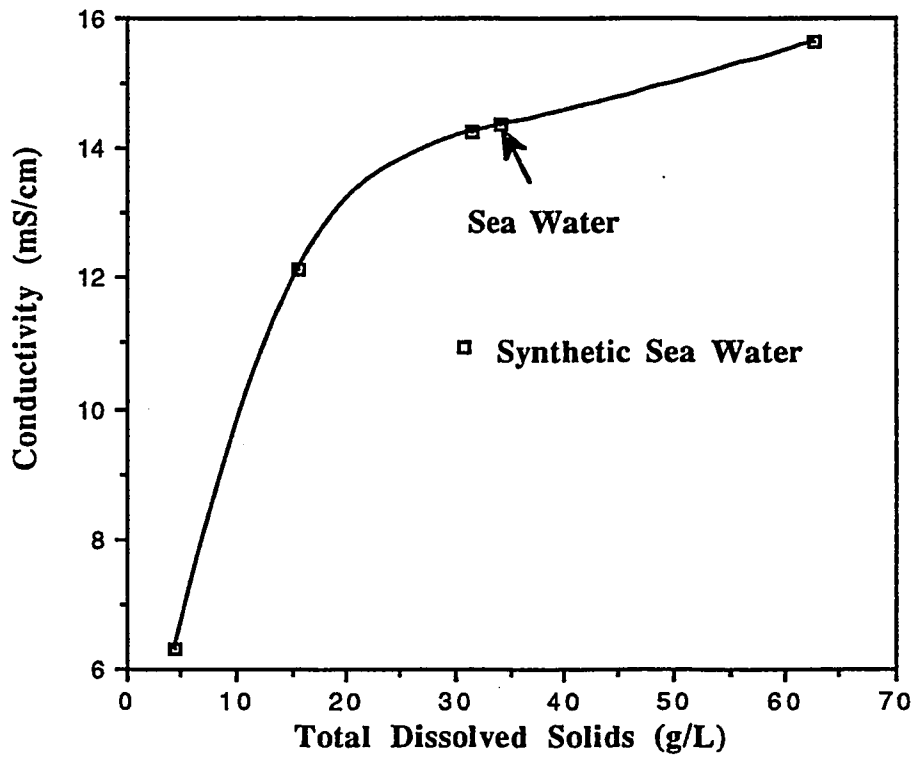


Figure 4.9 Conductivity of synthetic and natural sea waters

tricity is defined accordingly as a constant divided by the amount of chlorine in gas phase. This ratio R1 varies with the amount of chlorine in gas phase. The ratio of hydrogen to total chlorine (mol/mol) is a measure of the extent of Cl_2/O_2 evolution and it is a function of the current density, chloride concentration, and coulombs of electricity passed.

4.3.1 Hydrogen to Total Chlorine

Total chlorine is defined as the total amount of chlorine evolved at the anode, which includes chlorine in gas phase, and chlorine available in the liquid phase in the form of free-chlorine, hypochlorites, and chlorites. The ratio of H_2 to total Cl_2 is referred to as R2.

In figure 4.10, the change in R2 for 1000 C with current density is shown for sea water. The value of R2 ranges from 1.22 - 1.4 depending on current density with the highest ratio at the lowest current density (25.26 mA/cm^2).

In figure 4.11 (curve b) the ratio R2 decreases at low current densities since the total chlorine evolved is low due to the evolution of oxygen which is favorable at low current density as explained by Bockris⁽¹⁾. However, for low chloride levels (278.3 mmol/L), curve a, chlorine evolved is low and hence the ratio R2 is higher than for the case of 556 mmol/L. The best explanation for the sharp increase at 100 mA/cm^2 is that chloride ions are limited by mass transfer and hence chlorine evolved is lowered. The quantity of oxygen evolved with chlorine could be calculated from the coulombs used for production of oxygen

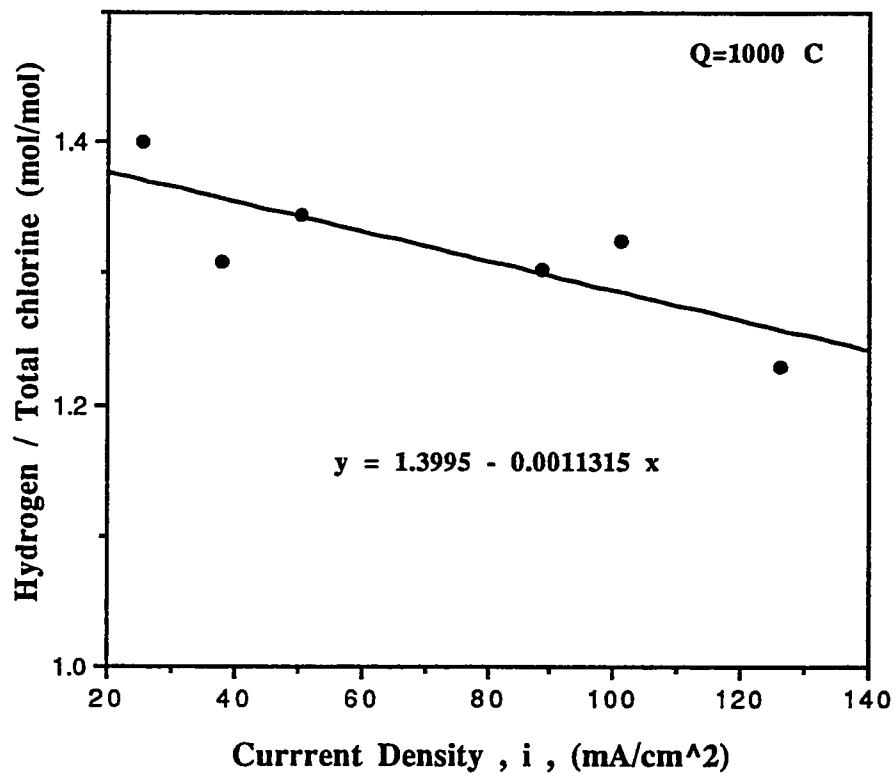


Figure 4.10 Hydrogen to total chlorine vs. current density for sea water

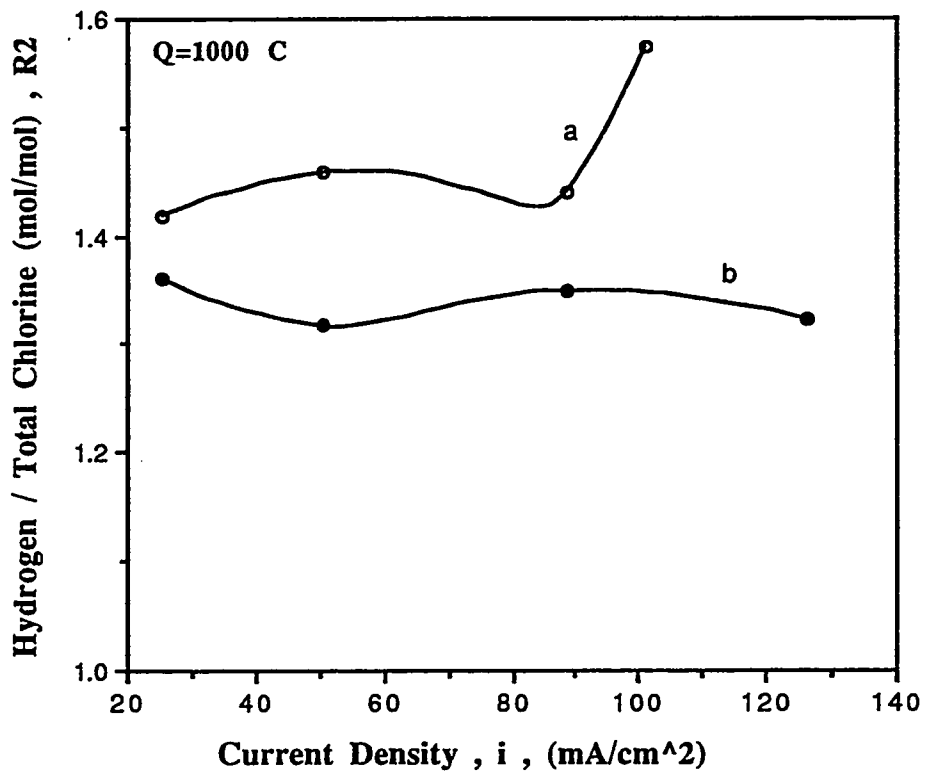


Figure 4.11 Hydrogen to total chlorine vs. current density for synthetic sea water
 (a) a solution of 278.3 mmol/L, S7
 (b) a solution of 556 mmol/L, S6

(see Appendix-A for similar calculations) and Cl_2/O_2 (mol/mol) ratio is 4.6. The ratio R2 increased to 1.58 (approximately). This ratio should be constant if hydrogen and chlorine increase proportionally with quantity of electricity. Although this is the case for hydrogen since there is no other competing reaction at the cathode and no problem with the availability of water, the case is different for the anode, where chlorine and oxygen compete and the availability of Cl^- ions is limited by the transfer from the bulk of the solution⁽¹⁾ to the anode. For these reasons, continuing the electrolysis process results in a higher hydrogen to chlorine ratio, and this explains the value of 1.32 at 1000 C and 1500 C.

Figure 4.12 shows the effect of change of concentration on R2 for different voltages for 1000 C. At concentrations < 600 (mmol/L) there is a sharp decrease of R2 with increasing Cl^- level, while at $\text{Cl}^- > 600$ (mmol/L) the effect of concentration is insignificant since these concentrations are high enough to avail Cl^- ions at the anode. The behavior of R2 with chloride level is an exponential decay. The ratio R2 and chloride concentration (mmol/L) are related by the equation :

$$R2 = 5.762 - 11 \log C$$

4.3.2 Hydrogen to Chlorine in Gas Phase

The effect of current density as well as quantity of electricity on hydrogen to chlorine ratio in gas phase R1 in sea water electrolysis is shown in figure 4.13. The ratio R1 is related to the quantity of electricity, Q, by the relation :

$$R1 = 922.99 - 289.92 \log Q .$$

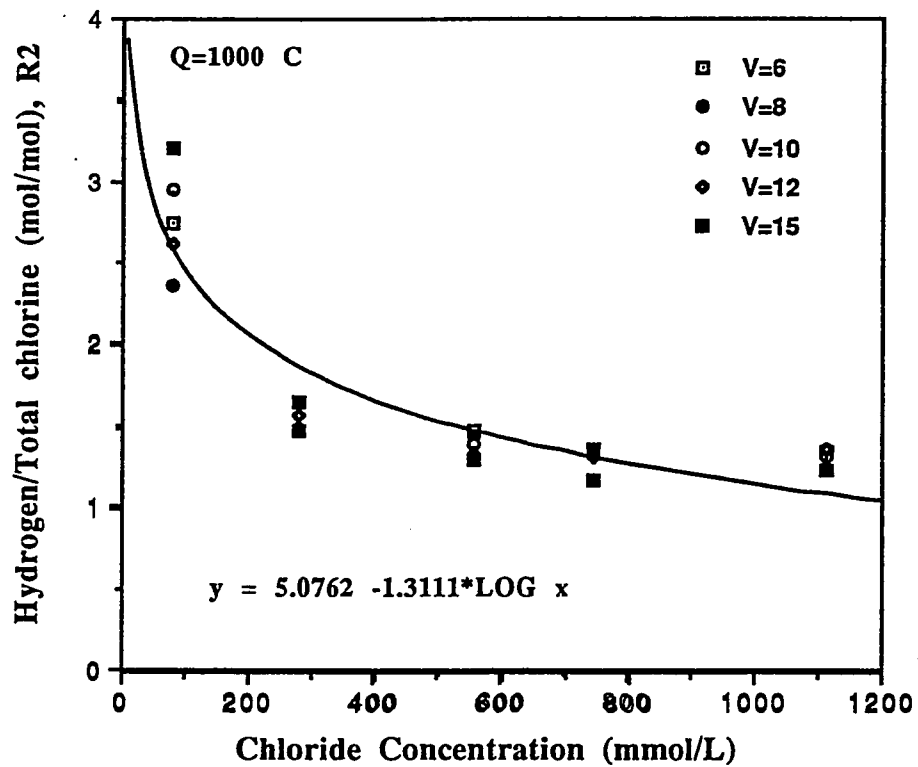


Figure 4.12 Hydrogen to total chlorine vs. chloride concentration for synthetic and natural sea waters at different voltages

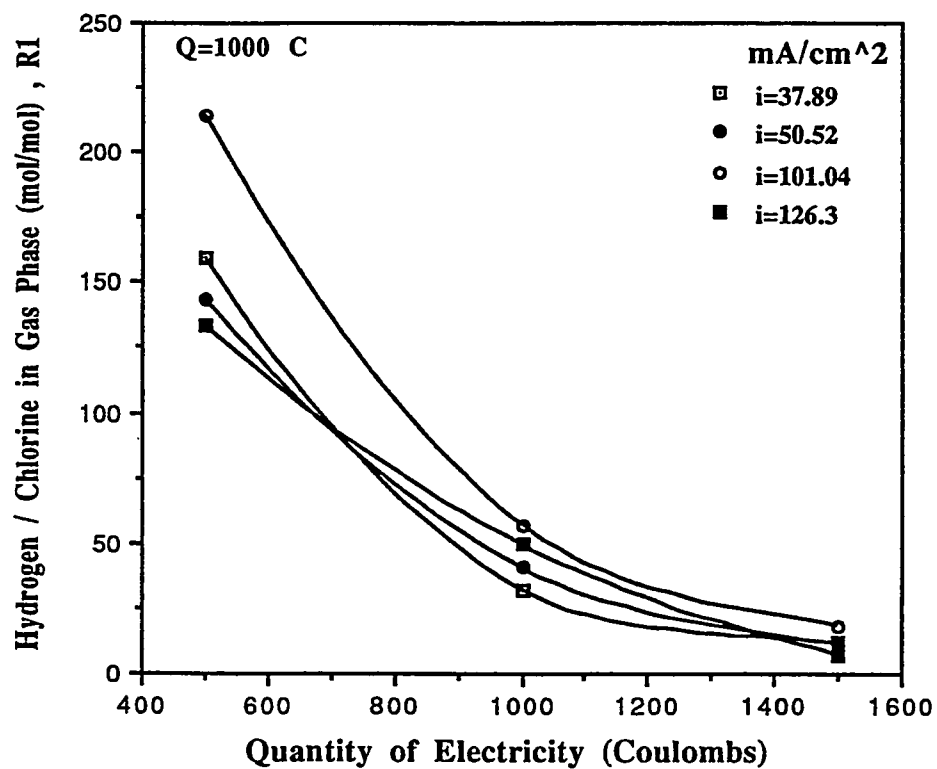


Figure 4.13 Hydrogen to chlorine in gas phase vs. quantity of electricity for sea water at different current densities

At low quantities of electricity (500 C) the chlorine in the gas phase is low compared to that evolved at 1500 C for reasons mentioned in section 4.2.1 above, and this explains the behavior of R1 with current density for different quantities of electricity which is shown in figure (4.14) .

The effect of chloride concentration on R1 at different current densities is shown in figure 4.15 for natural and synthetic sea waters. At low current density (25.63 mA/ cm²) R1 is approximately 35 and is concentration independent. At 50.52 (mA/ cm²) R1 ranges from 50 - 70 with high values at low chloride levels since chlorine evolved is low, but for 88.41 (mA/ cm²) R1 increases for Cl⁻ (800 mmol/L) and drops sharply after that, and this behavior is due to variations of chlorine evolved in gas phase with current density. A summary of correlations obtained in the previous sections is given in Table 4.2.

4.4 CHLORINE EFFICIENCY

The quantity of electricity passed (either 500, 1000 or 1500 C) was monitored by measuring the current and time knowing that:

$$Q = A \int_0^t i t dt \quad (4-1)$$

where

Q = quantity of electricity passed, over a period of time, t in coulombs

i = current passing through the cell, A/cm²

A = electrode surface area, cm²

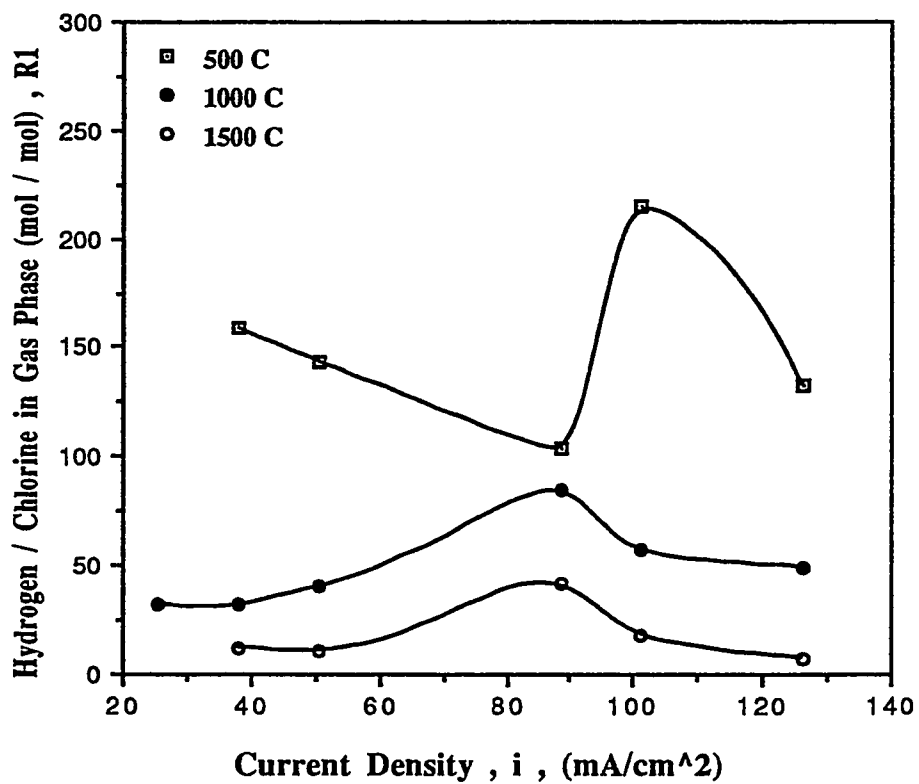


Figure 4.14 Hydrogen to chlorine in gas Phase vs. current density for sea water at different coulombs

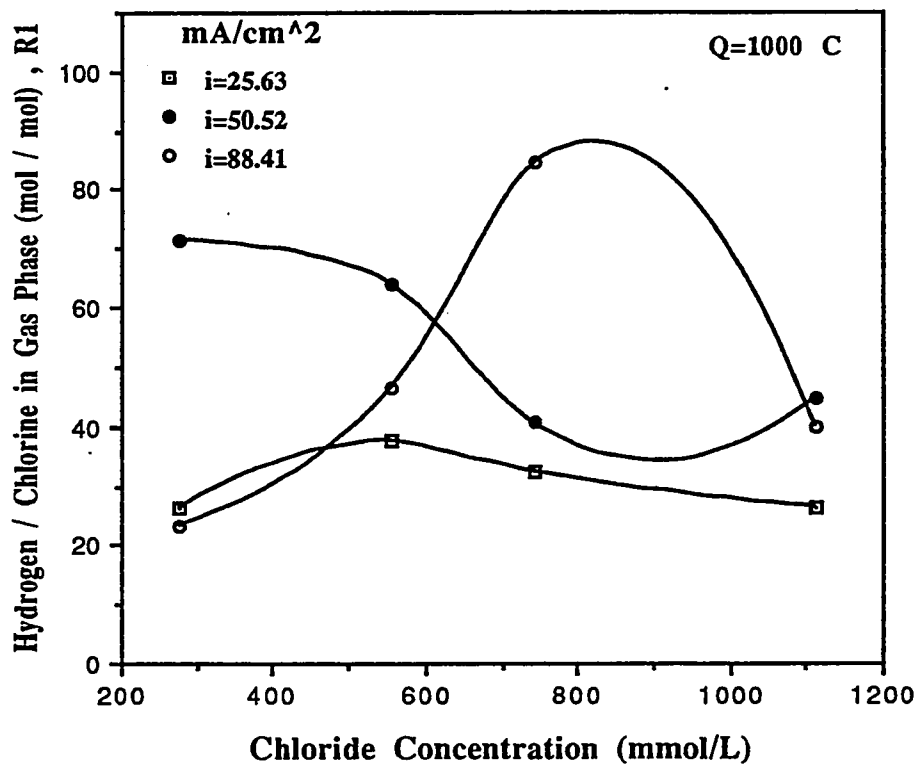


Figure 4.15 Hydrogen to chlorine in gas phase vs. chloride concentration for synthetic and natural sea waters at different current densities

Table 4.2 Modeling and correlations

Description	Correlation	Range of Applicability	Correlation Coefficient, R ²
Hydrogen production rate	$HPR = - 0.20832 + 0.7236 i$	i : 25 - 126	0.999
Total chlorine	i) $Cl_T = - 3.0918 + 3.8090 \log C$	C : 79.6 - 1113.2 Voltage : 6 - 15 V	i) 0.921
	ii) $Cl_T = 0.51913 + 0.00737913 Q$	Q : 500 - 1500 C	ii) 0.997
Hydrogen to chlorine in gas phase, R1	$R1 = 922.99 - 289.92 \log Q$	Q : 500 - 1500 C	0.959
Hydrogen to total chlorine, R2	$R2 = 5.0762 - 1.311 \log C$	C : 79.6 - 1113.2	0.882
Conductivity	$Cond. = 1.4235 + 8.3304 \log TDS$	TDS : 4.48 - 62.7	0.971

HPR Hydrogen Production Rate, (mL/hr)

i Current density, (mA/cm²)

Cl_T Total chlorine (mmol)

C Chloride level (mmol/L)

Q Quantity of electricity, (C)

R1 Ratio of hydrogen to chlorine in gas phase, (mol/mol)

R2 Ratio of hydrogen to total chlorine , (mol/mol)

TDS Total Dissolved Solids, (g/L)

Cond. Conductivity, (mS/cm)

The current efficiency is then given by

$$E_c = \frac{V_R (C_f - C_i) n F}{A \int_0^t i dt} \quad (4-2)$$

where

V_R = Volume of the reactor

C_i and C_f are the initial and final concentrations of chlorine in the cell.

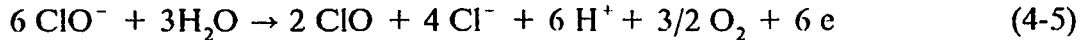
The value of $V(C_f - C_i) n F$ for chlorine if total chlorine evolved as free chlorine, chlorite and hypochlorite was easily determined by iodometric titrations using ascorbic acid. Chlorine current efficiency decreases mainly (oxygen evolution) due to the anodic discharge of hydroxide ions,



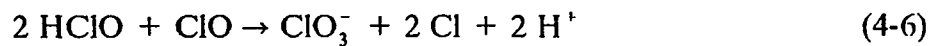
This reaction competes with anodic chlorine evolution. In addition, a small inefficiency can result from the chemical reaction



There are, however, several competing reactions which contribute to cell inefficiencies (oxygen evolution). Chlorate may be formed by either anodic oxidation of hypochlorite,



or by the chemical reaction between hypochlorite ion and hypochlorous acid,



Both of these reactions have been studied extensively^(33,34), because they are significant in the electrolytic production of chlorate. The chemical chlorate formation equation (4-6) proceeds very slowly at room temperature and a basic pH value. This reaction is, therefore, insignificant because cells do not operate over 40° C, and normally equilibrate near pH 10 for solutions in the range of chloride level studied (14-200% of sea water chloride level), as shown in section 4.6 below.

Separate efficiencies for oxygen and chlorine evolution from low chloride solution is difficult to determine using conventional instrumental techniques. Although individual voltammetry peaks for chloride oxidation can be obtained under certain conditions, the two oxidation reactions usually occur simultaneously with no clear definition between them. For this reason, a batch electrolysis is useful where total voltage is plotted against % chlorine current efficiency for synthetic and natural sea water (Figure 4.16). Once the Faradaic efficiency for chlorine is established in raw or synthetic sea water, oxygen evolution can be assumed to consume the balance of the anodic current⁽¹⁸⁾. Results for sea water at different quantities of electricity were shown in figure 4.17a.

A comparison of chlorine current efficiency with the previous work of Bennet⁽¹⁸⁾ is shown in figure 4.17b. Bennet results are higher than the current research mainly because of higher current density and circulation of electrolyte applied by Bennet. The method of chlorine analysis used by Bennet used iodometry with thiosulfate as the reducing agent, and this could be a source of errors.

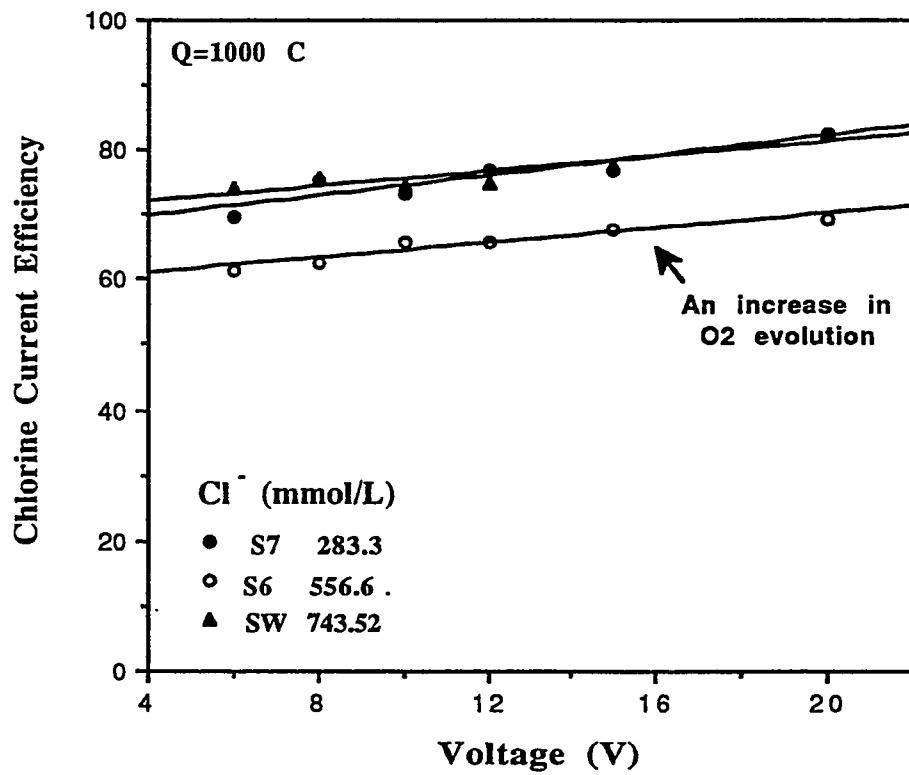


Figure 4.16 Chlorine current efficiency vs. voltage for synthetic and natural sea waters

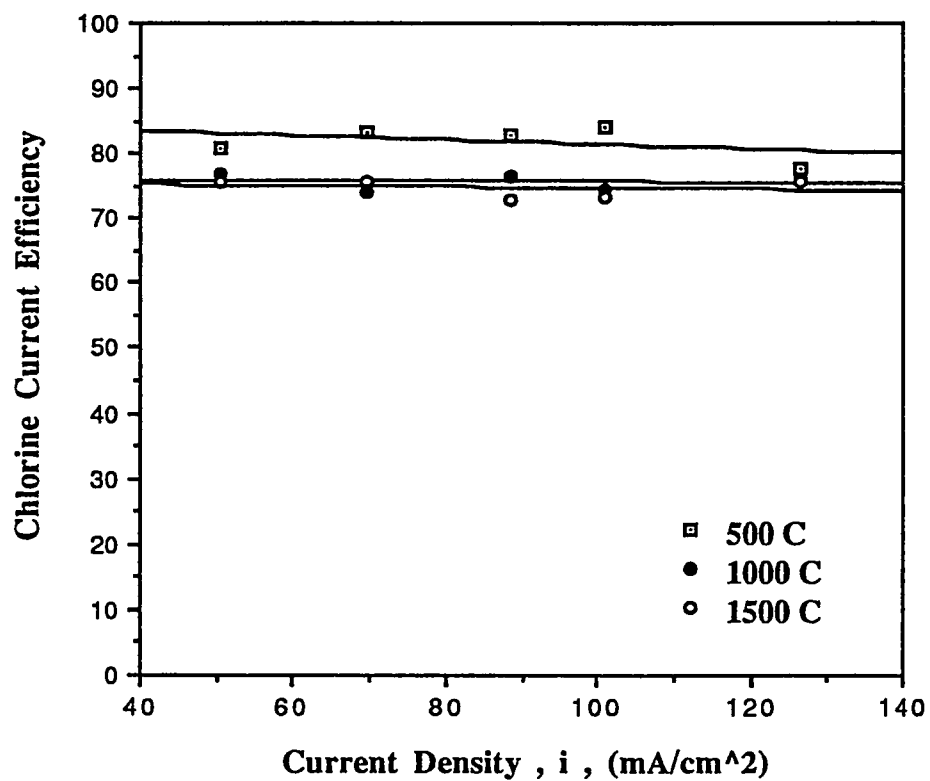


Figure 4.17a Chlorine efficiency vs. current density for sea water at different coulombs of electricity

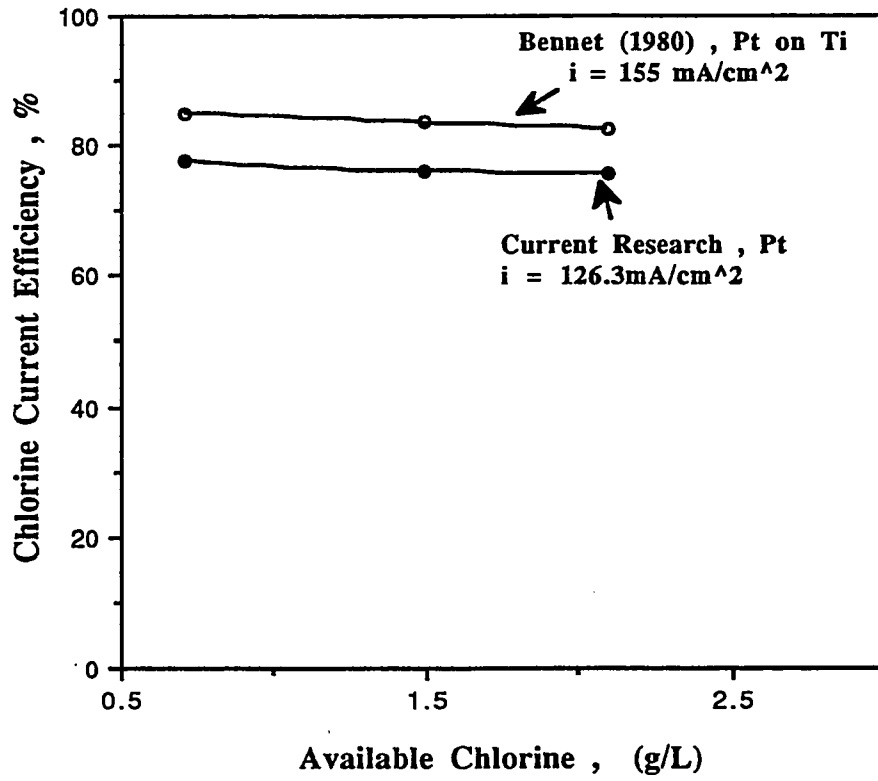


Figure 4.17b Comparison of chlorine current efficiency for sea water with previous work

This work considers iodometry with ascorbic acid which has no errors as explained by Erdey⁽³²⁾. Reproducibility was found to be less than 0.5%.

Although chlorine is not a desirable product in the sea water electrolysis, chlorine efficiency is taken care of since the analysis was done for chlorine knowing that the balance of current passed is used for the production of oxygen.

Figure 4.17a shows the effect of current density and quantity of electricity on chlorine efficiency. At low quantity of electricity i.e 500 C the efficiency is high (82%) and is independent of current density i.e. low oxygen. For the case of 1000 C and 1500 C the efficiency decreases to 76% for the limitations of the transfer of Cl^- ions from the bulk of the solution to the electrode, i.e. increase in oxygen evolution. Figure 4.18 shows the effect of chloride concentration on chlorine efficiency at different current densities. At chloride levels > 500 (mmol/L) and current densities > 50 mA/cm² the efficiency is independent of chloride concentration as well as current density, (about 76%), while at low current density (25.26 mA/cm²) the efficiency drops since more oxygen is evolved at low current densities. For the lowest chloride level (278.3 mmol/L) the efficiency is independent of current density and it is approximately 70%. This decrease is an evidence that the current density is approaching the diffusion limiting current for chloride oxidation

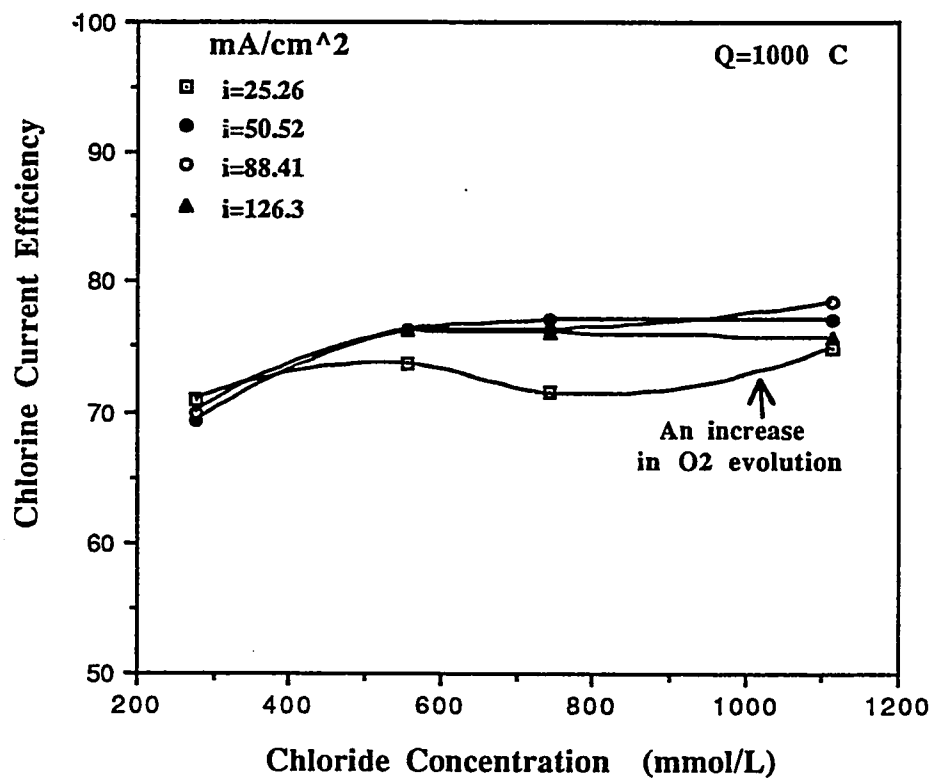


Figure 4.18 Variation of chlorine efficiency with chloride concentration for synthetic and natural sea waters at different current densities

4.5 MAGNESIUM ADHERED PRECIPITATE DURING ELECTROLYSIS

In determining the effect of the operating parameters on the cathodic fouling process during synthetic and natural sea water electrolysis, both individual and combined contributions have to be considered. The cell design facilitates separation of reaction products, but there was no circulation of the electrolyte.

For the range of the current densities ($25 - 126 \text{ mA/ cm}^2$) used in these experiments, hydrogen evolution at the cathode obscured the visibility of the electrode and the adhered precipitate could not be detected until the electrolysis was stopped .

A curve of electrolyte conductivity measurements versus total dissolved solids (TDS) is shown in figure 4.9. Conductivity increases with increasing TDS. The value of conductivity for natural sea water is approximately equal to that corresponding to synthetic sea water. As a result of the asymptotic behavior of conductivity with TDS, TDS greater than 62.7 g/L (two times normal sea water TDS) would provide only marginal improvement in electrolyte conductivity. Correlation of conductivity and TDS is given in Table 4.2. The initial pH values of these solutions were about 6 for all solutions of concentrations greater than 4.48 g/L , and for 4.48 g/L solution it was 6.34, as shown in figure 4.19 .

Electrolyte concentration have a marked effect on the formation of insoluble precipitates as shown in figure 4.20 . The results are for a constant current densities of 25.26 , 50.52 , and 88.41 mA/ cm^2 at 1000 C of electricity. The mass of

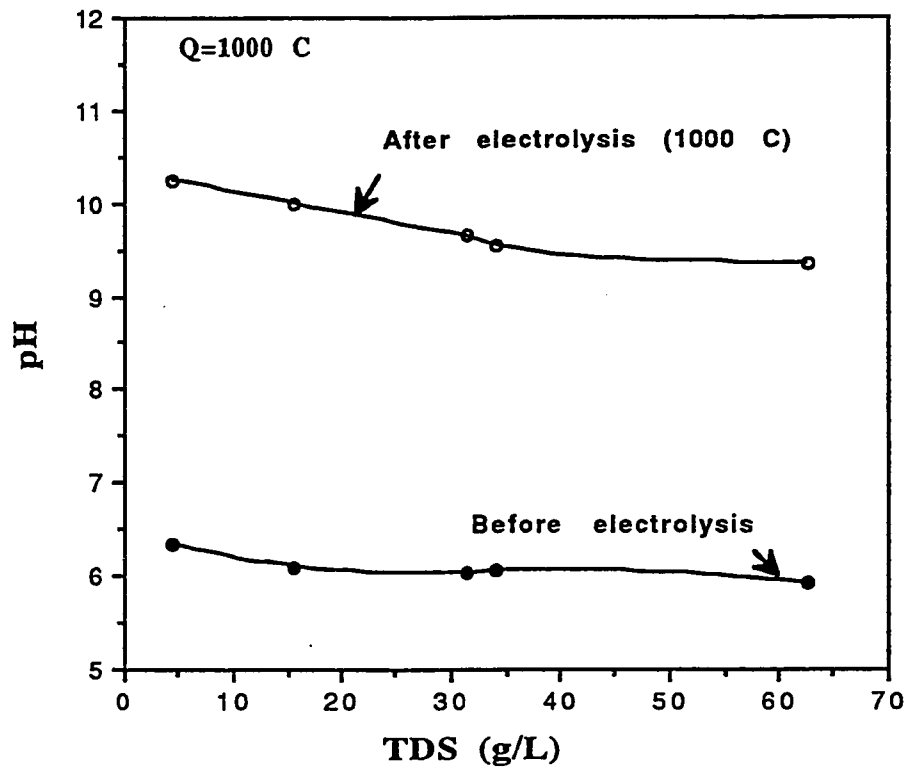


Figure 4.19 pH vs. chloride concentration for synthetic and natural sea waters before and after electrolysis

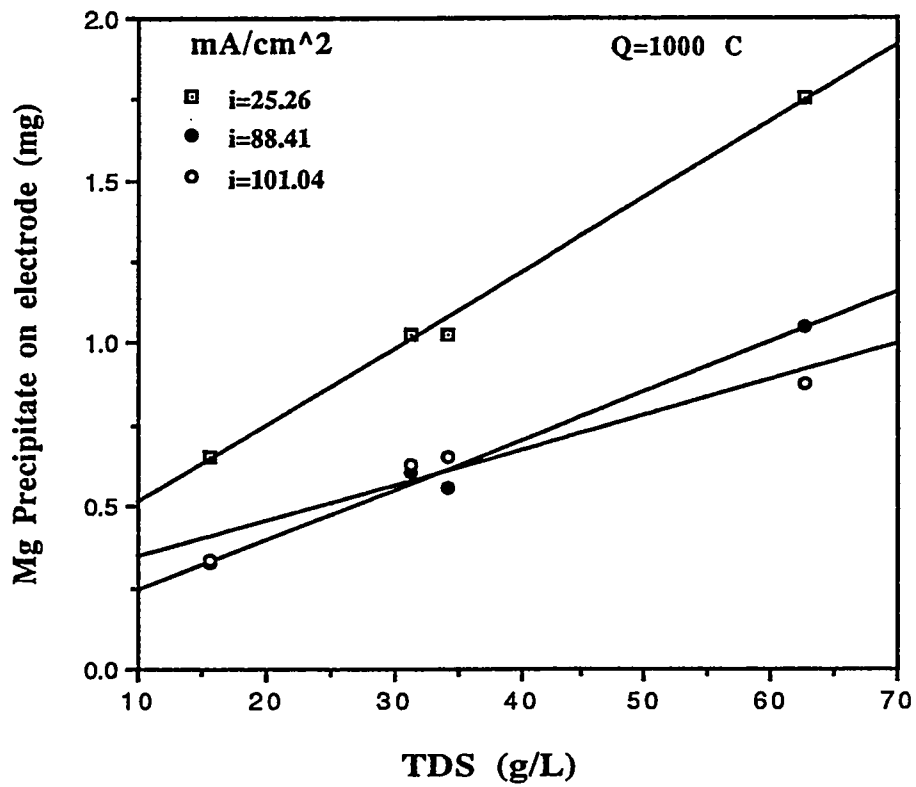
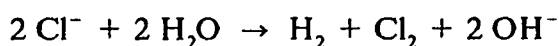


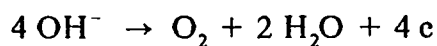
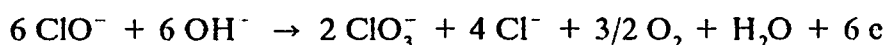
Figure 4.20 Mg precipitate on cathode vs TDS for synthetic and natural sea waters at different current densities

Mg precipitate adhering to the electrode was obtained by dissolving the precipitate in 10 mL of 1 M HCl solution and then Mg concentration was determined by AA. The same type of precipitate reported by Williams⁽²⁰⁾ (Mg(OH)₂ and Ca(OH)₂) were found. The Mg precipitate increases linearly with total dissolved solids (TDS) in solution .

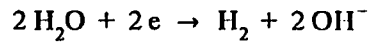
The composition of the electrolyte also affected the change of pH value during electrolysis. It increased from approximately pH 6 for the initial values to approximately pH 9.4 - pH 10.3 for 1000 C as shown in Figure 4.19 The increase in pH is due to the hydrogen evolution at the cathode as well as the escape of chlorine from the solution at the anode . The overall reaction is :



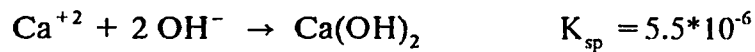
However secondary reactions involving chlorine or the formation of oxygen tend to lower the pH value by consuming the hydroxide ions (or liberating the hydrogen ions in acid solutions) . Three such reactions are⁽¹⁹⁾ :



without the loss of chlorine these reactions would neutralize the hydroxide formation at the cathode :



It is clear from figure 4.19 that the higher initial TDS gives smaller pH increase after electrolysis and this is accounted for by the amount of precipitate formation from the reactions :



From the above solubility product values for $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ it is clear that $\text{Mg}(\text{OH})_2$ is the dominant precipitate. As an identical number of coulombs were used for each run and the initial pH values were approximately the same (except for the 4.48 g/L solution), the principal cause for the variation in the resulting pH values must be the amount of precipitate formed .

The effect of current density on precipitate formation was shown in figure 4.20 for 1000 C at three different concentrations of synthetic and natural sea waters. For a current density of 50.52 mA/cm² the precipitate formed is always showing higher values for all concentrations compared to other current densities. This is due to high local pH values of the catholyte obtained at low current density because of the poor circulation of the solution in the cell which is a favorable condition for homogeneous precipitation⁽³⁵⁾ . For higher current densities the precipitate is lower than the previous case. This is a direct result of the decrease in the pH of the catholyte due to the increased current density, increased electrode scouring with increased rate of hydrogen evolution at the cathode surface, and the decrease in the effective diffusion layer

Figure 4.21 shows the amount of Mg precipitate versus current density for natural sea water electrolysis at different coulombs of electricity. The higher the quantity of electricity the higher the precipitate formed which is a direct result of more time of electrolysis. All curves are showing a rapid decrease in precipitate with increased current density for reasons mentioned above. However, higher current densities showed an increase in precipitate with the increase in TDS, because of the improved mass transfer. The current density affects several parameters at once. In the case of increased current density the effect of improved mass transfer was probably offset by the decrease in the pH at the surface.

In order to explain these effects, it is useful to consider the hydroxide concentration gradient. In the bulk, the hydroxide concentration is essentially constant and the $\text{pH} < 9$, and hence no magnesium hydroxide precipitation occurs. The increase in hydroxide level is confined to the adjacent layer near the electrode surface. Therefore, any increase in the adjacent layer simply increases the hydroxide concentration gradient. Thus the reaction zone, that is the region where the pH level is sufficiently high to cause precipitation, is reduced. Since the precipitation process is slow, then decreasing the adjacent layer will decrease the total amount of the reaction, i.e. decrease Mg precipitate as shown in figure 4.21. The slight increases observed with 1000 C and 1500 C is mainly due to enhancement in mass transport with increased current density and quantity of electricity. This type of behavior is often characteristic of a diffusion-controlled reaction.

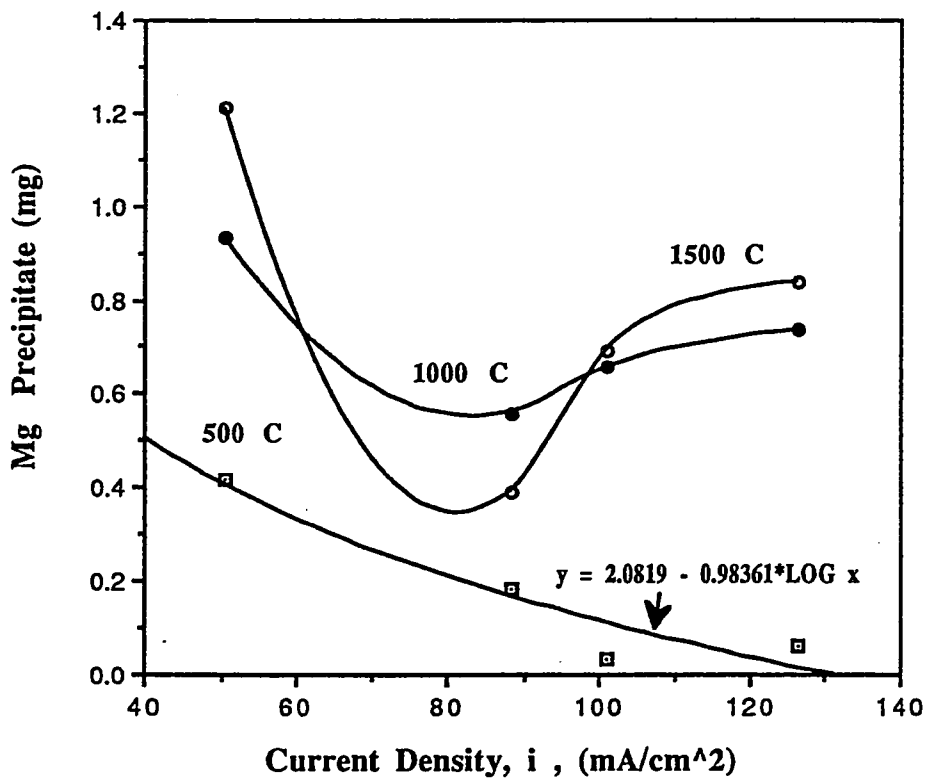


Figure 4.21 Mg precipitate vs. current density for sea water for different coulombs of electricity

4.6 POLAROGRAMS FOR SALINE WATER

The process of hydrogen liberation has attracted special attention due to its great practical significance. The overpotential of hydrogen liberation on an electrode is often very large. In most cases it exceeds the magnitude of the electrolyte concentration overpotential, as well as the discharge potentials of ions on various electrodes. The latter is highly important in many electrochemical processes⁽²¹⁾. In the electrolysis of aqueous electrolytes, hydrogen ions are present in the solution along with ions of the electrolyte. If there were no hydrogen overpotentials, hydrogen ions would discharge on the electrode when an emf is applied. Actually, since this overpotential is large, the process starts with the discharge of other ions. A noticeable liberation of hydrogen occurs only when the emf substantially exceeds the discharge potential of other ions. The discharge of alkali metal ions on a mercury electrode (from a solution containing alkali metal ions and H^+ ions), and the large emf necessary for the electrolytic decomposition of water is related to this effect.

It should be noted that the over potential required for the discharge of hydrogen on an electrode is not constant, but is a function of the current density. It has been found experimentally⁽³⁵⁾ that, at extremely low current densities, the hydrogen overpotential is a function of current density in accordance with the relation :

$$\eta_H = \text{Const. } i \quad (4-7)$$

At high current densities, the hydrogen overpotential is expressed by the Tafel formula :

$$\eta_{H} = a + \frac{RT}{\alpha F} \ln i \quad (4-8)$$

Figures 4.22a and 4.22b shows the polarogram for natural sea water and synthetic sea water respectively. The surface area of the mercury drop was calculated from the average drop weight of 15 mercury drops with the assumption of a spherical shape, and using the density of mercury at 20° C . The average surface area of the drop was found to be 0.02204 cm² .

The decomposition voltage, E_D , was obtained by extrapolating the linear part of the graph to the datum line of the plot, and then reading the corresponding E value. The E_D was found to be 1.87 V for natural sea water and 1.91 V for synthetic sea water versus Ag/AgCl electrode. The difference is mainly due to other elements not catered for in the simulated composition of the synthetic sea water, and the variations in the pH values. The E_D values for all solutions studied was found to be in the range of 1.82 - 1.92 V corresponding to pH values between 5.92 - 7.86 as shown in Table 4.3. Polarograms for other solutions were shown in Appendix-C.

If there is no electrolysis, the current should be zero. However, there is a finite current. This is called the residual current, and have higher values for the natural sea water. This residual current is due to two factors. The most important one is the charging current, required for the charging of the so-called elec-

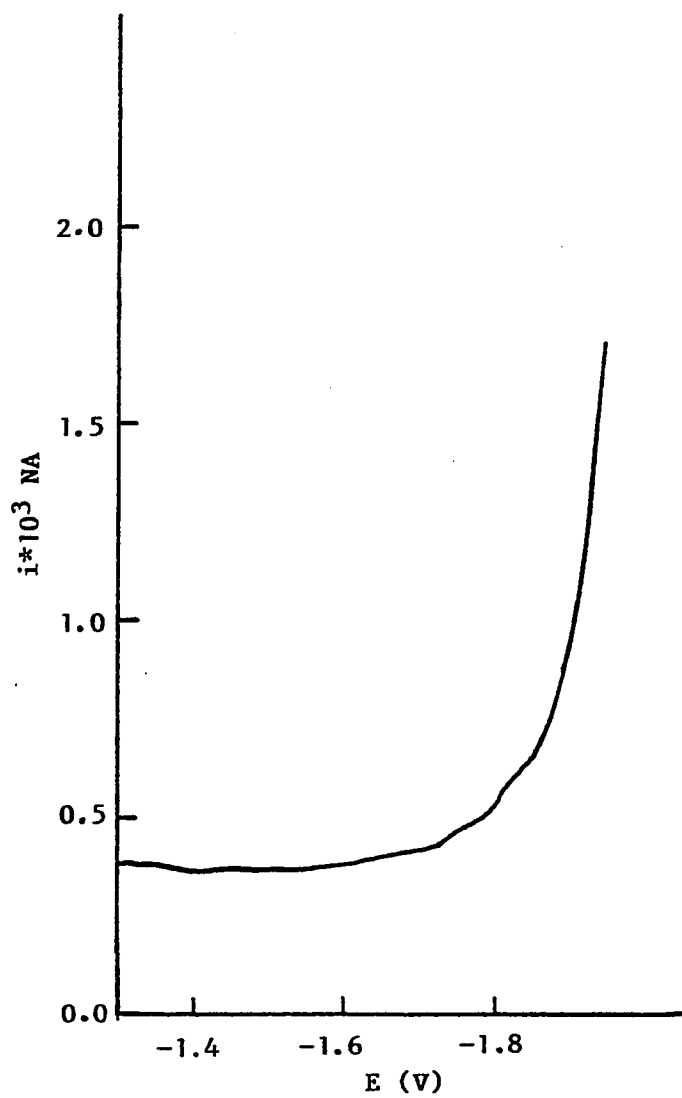


Fig. 4.22a Polarogram for natural sea water

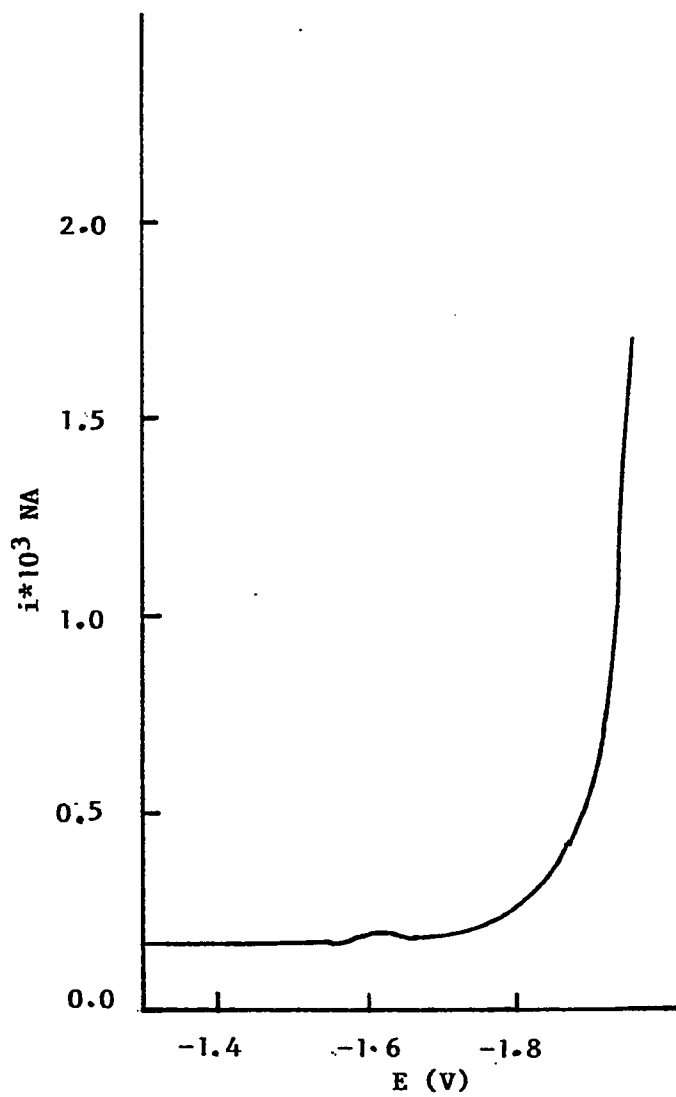


Fig. 422b Polarogram for synthetic sea water(31.35 g/L)

Table 4.3 Decomposition voltage of saline water.

Salt Concentration (g/L)	Composition	-E_d, (V) (vs Ag/AgCl)	pH
3.78	NaCl	1.920	7.86
13.21	NaCl	1.880	6.75
26.42	NaCl	1.885	6.39
52.83	NaCl	1.850	6.29
4.48	NaCl + MgCl ₂	1.935	6.34
15.67	NaCl + MgCl ₂	1.910	6.10
31.35	NaCl + MgCl ₂	1.910	6.04
34.22	Sea Water	1.870	7.95
62.70	NaCl + MgCl ₂	1.820	5.92

trical double layer at the surface of the mercury electrode, where the electrode acts as a capacitor. The other factor contributing to the residual current is the presence of impurities and this is quite clear for the case of natural sea water as shown in figure 4.22a.

4.7 USE OF DIRECT SOLAR ENERGY

Natural sea water was electrolyzed using the DC obtained by solar photovoltaic cells. The experiment was carried by connecting the electrolytic cell directly to the solar panel. Solar panel output, i.e. voltage and current, was measured and obtained as power per unit area. Details of solar panels were given in chapter three. Measured values of solar radiation were obtained from the weather station of the Research Institute for the time of the experiment.

Figure 4.23a shows the solar cell output in W/m^2 versus solar radiation. The solar cell output showed a decrease in the morning (9 - 11 a.m.) with the increase of solar radiation. However in the afternoon hours the solar panel output was slightly increasing with the decrease in solar radiation. This is mainly due to wind effects. The average wind speed showed an increase in the morning over the afternoon hours, and reached its highest value for the day at 10 a.m.(4.1 m/s). This cooling effect is due to natural and forced convection, and it is the reason for the decrease in the output of the solar cell observed in figure 4.23a since solar panel output decrease with the increase in temperature. The average wind speed during day hours was shown in figure 4.23b .

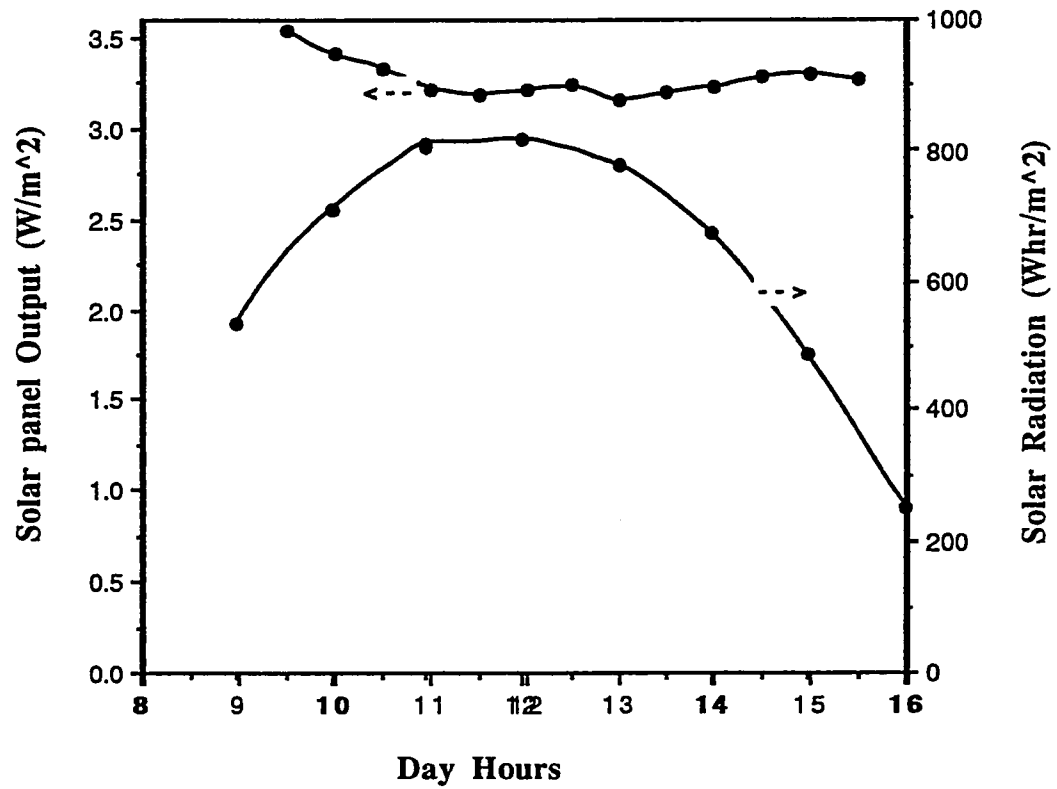


Figure 4.23a Variation of solar panel output with solar radiation during day hours on 19 / 11 / 91

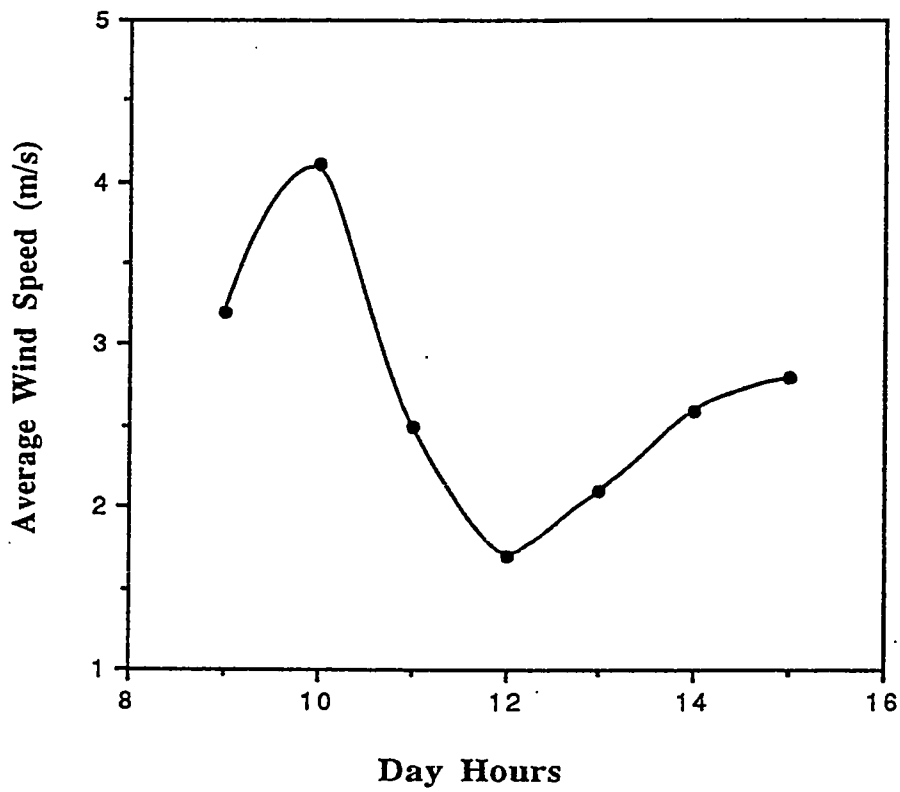


Figure 4.23b Variation of wind speed during day hours on 19 / 11/1991

The variations of the solar radiation with temperature for the same day was shown in figure 4.24, and as expected similar behavior was obtained.

The hydrogen production rate was measured on hourly basis and as expected it follows the increase or the decrease in solar cell output as shown in figure 4.25.

In practice specific solar generator characteristic should be studied for optimum voltage operation to achieve maximum utilization of power generated at specific solar radiation and cell temperature . Such characteristic i-V curves are provided with the cell for different conditions of radiation and temperature, and conditions for electrolysis will be decided accordingly .

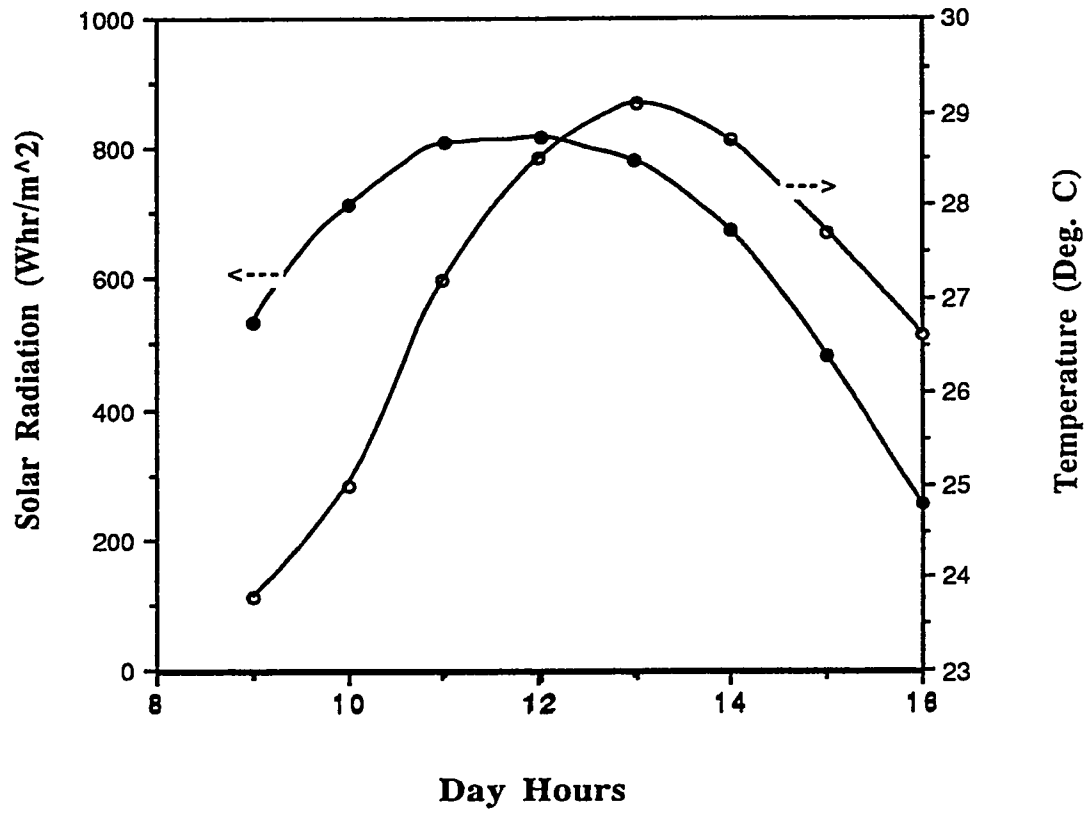


Figure 4.24 Variation of solar radiation with temperature during day hours on 19 / 11 / 91

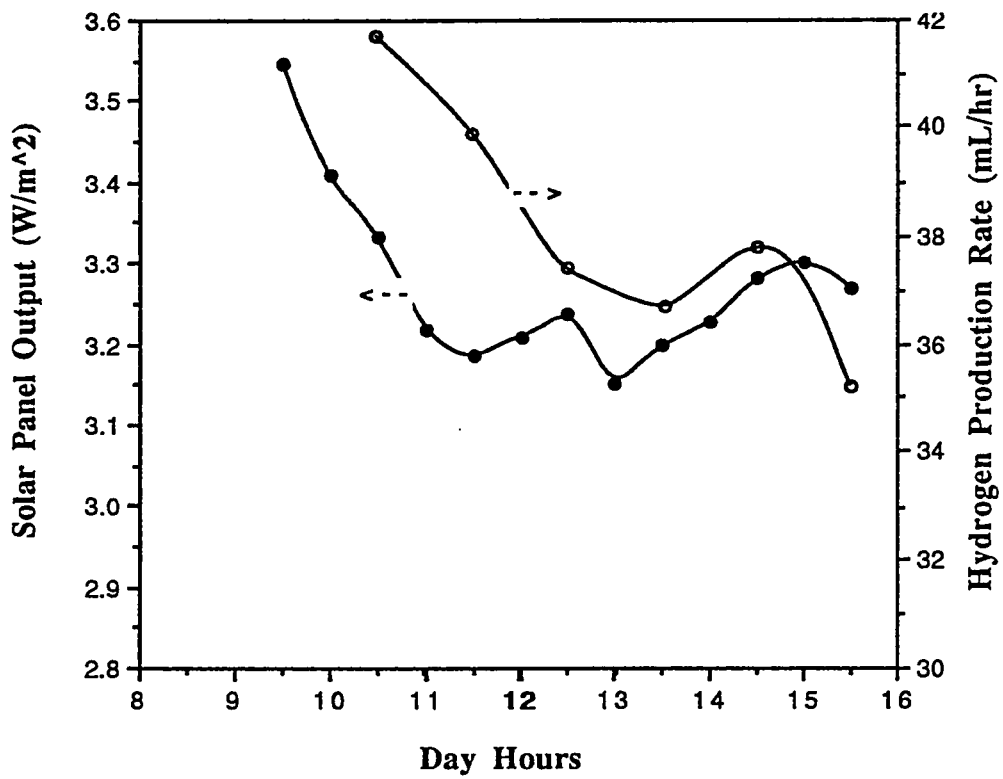


Figure 4.25 Solar panel output & hydrogen production during day hours on 19 / 11 / 91

CHAPTER FIVE
CONCLUSIONS AND RECOMMENDATIONS

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

During the course of investigation on the electrolysis of saline water, and within the experimental conditions reported on the type of cell used, and the range of salinity studied; the following are the most important conclusions and recommendations.

5.1 CONCLUSIONS

The most important conclusions are :

- (1) Hydrogen was produced at 99% current efficiency.
- (2) The TDS of saline water used has a direct impact on the rate of hydrogen production as observed from previous results. Accordingly a high salinity water (67.2 g/L) when electrolyzed will give the highest rate of hydrogen production compared to other salinities under the same voltage. The shortcomings of using this saline water, on the other hand, are the noticeable formation of precipitates on the cathode.
- (3) The total chlorine produced in the cell is reported as a function of current density and coulombs. This is considered a novel experimental achievement. The relative Cl_2 / O_2 ratios could be obtained from the reported chlorine current efficiencies since the balance accounts for the evolution of oxygen.

Chlorine is produced at current efficiency of 75 - 82 % for sea water. This is considered to be high, compared to 95 - 97% for brine electrolysis. Lower concentrations resulted in current efficiencies as low as 42% for 1000 C due to mass transfer limitations of chloride ion to the anode.

- (4) Chlorine evolution at the anode replaces oxygen even for chlorides concentrations lower than those of sea water. This shows how mass transfer and kinetics combine to make chlorine evolution the dominant anodic reaction product.
- (5) The amount of $Mg(OH)_2$ precipitates, which is the most serious corroding deposit, varies with current density and coulombs of electricity. Cell operation at low coulombs ($< 500 C$) and high current densities ($90 - 110 mA/cm^2$) resulted in a minimum precipitate on the cathode.
- (6) Sea water, and other types of available saline water, could be a source of hydrogen fuel for tomorrow's world.

5.2 RECOMMENDATIONS

The following are our recommendations for further work :

- (1) The procedure used for the analysis of chlorine has no errors as explained by Eredy, and we recommend its use for further or similar researches.
- (2) Further work should investigate the role of solution mixing in reducing precipitate on the cathode. The mixing acts in two favored directions. The

first is to reduce the concentration overpotential due to concentration gradient in the electrolyte. The second is to reduce the pH at the cathode. A pH of the catholyte of less than 9 will prohibit formation of precipitate formation.

- (3) Furthermore, cell performance should be studied at different coulombs and temperatures in addition to other electrode materials.
- (4) The interaction between increased mass transfer, due to increased current density, and the decrease in pH because of the decrease in the effective diffusion layer could be studied for other cells to select the optimum conditions for minimizing the precipitate.
- (5) The current practice in sea water electrolysis, utilizes chlorine in a form of hypochlorite for the treatment of sea water used in secondary oil recovery only and vents hydrogen to the atmosphere. We recommend the electrolysis of sea water for the production of hydrogen in many parts of the arab world using solar energy which is abundant as well.
- (6) We recommend the use of these results as basis for further work in saline water electrolysis.

NOMECLATURE

A	Electrode surface area
a	Constant of Tafel formula
a_{H^+}	Activity of hydrogen ions
C_f	Final concentration of chlorine
C_i	Initial concentration of chlorine
Cl_T	Total chlorine evolved
E	Voltage
E_a	Anode potential
E_c	Cathode potential
E_D	Decomposition voltage
E_s	Energy efficiency
E_{H_2}	Theoretical voltage for hydrogen evolution
E_i	Current efficiency
E_{O_2}	Theoretical voltage for oxygen evolution
E°	Decomposition voltage at standard conditions
E_p	Decomposition voltage at pressure P
E_r	Reversible voltage
E_v	Voltage efficiency
F	Faraday constant
G	Gibbs free energy
H	Enthalpy

HPR	Hydrogen Production Rate
i	Current density
i_l	Limiting current density
i_o	Exchange current density
IL_{max}	Maximum load current
K_{sp}	Solubility product
m	Amount of production at the electrode
n	Number of electrons transferred per molecule
P	Pressure
Q	Quantity of electricity passed
R	Gas constant
$R1$	Ratio of hydrogen to chlorine in gas phase
$R2$	Ratio of hydrogen to total chlorine
R_s	Electrical resistance
S	Entropy
t	Time of electrolysis
T	Temperature
U	Energy consumption
V	Volume
V_p	Volume of products
V_r	Volume of reactants
$V_{R.}$	Volume of the reactor
V_t	Actual voltage required for electrolysis

Z	number of moles
α	Transfer coefficient
η_a	Activation overvoltage
η_c	Concentration overvoltage
η_H	Discharge potential for hydrogen
η_t	Total overvoltage
ΔV	Change in volume
Θ	Electrochemical equivalent

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APPENDICES

APPENDIX-A
SAMPLE CALCULATIONS

APPENDIX-A
SAMPLE CALCULATIONS

1. HYDROGEN CURRENT EFFICIENCY

$$m = \theta \cdot I \cdot t \cdot E_i \quad (2-22)$$

where θ is the electrochemical equivalent ($\theta = .037607 \text{ g/Ah}$ for H_2).

From Fig. 4.1 the slope of the plot of hydrogen production rate versus current density is $85 \text{ (mL/hr)/120 mA/cm}^2$.

The pressure is 1 atm and the temperature is 23°C (296 K).

Then the current efficiency is given by:

$$\begin{aligned} E_i &= \frac{m}{\theta I t} \\ &= \frac{85 \text{ (mL/hr)} \cdot 2 \cdot 1.008 \text{ (g/mol Hydrogen)}}{0.037606 \text{ g/Ahr} \cdot 0.082 \text{ (atm lit/K mol)} \cdot 296 \text{ K} \cdot 120 \text{ (mA/cm}^2) \cdot 1.5835 \text{ cm}^2} \\ &= 99 \% \end{aligned}$$

2. Determination of Chlorine and Oxygen Efficiencies

$$Q = A \int_0^t i \, dt$$

Q = Quantity of electricity, C

A = Area of the electrode i = current density, mA/cm²

Current efficiency is given by:

$$E_i = \frac{V(C_o - C)ZF}{Q}$$

$V(C_o - C) = \text{moles of chlorine evolved}$

Total chlorine evolved at $101 \text{ mA/cm}^2 = 274.5 \text{ mg Cl}$

Coulombs of electricity used for chlorine production

$$= 0.2745 \times 96487 / 35.453 = 747 \text{ C}$$

Chlorine efficiency = $747/1000 = 74.7 \%$

Coulombs used for oxygen = $1000 - 747 = 253 \text{ C}$

Oxygen efficiency = $253/1000 = 25.3 \%$

chlorine / oxygen molar ratio = $747 / 253 = 2.95$

APPENDIX-B

EXPERIMENTAL RESULTS FOR NaCl SOLUTIONS

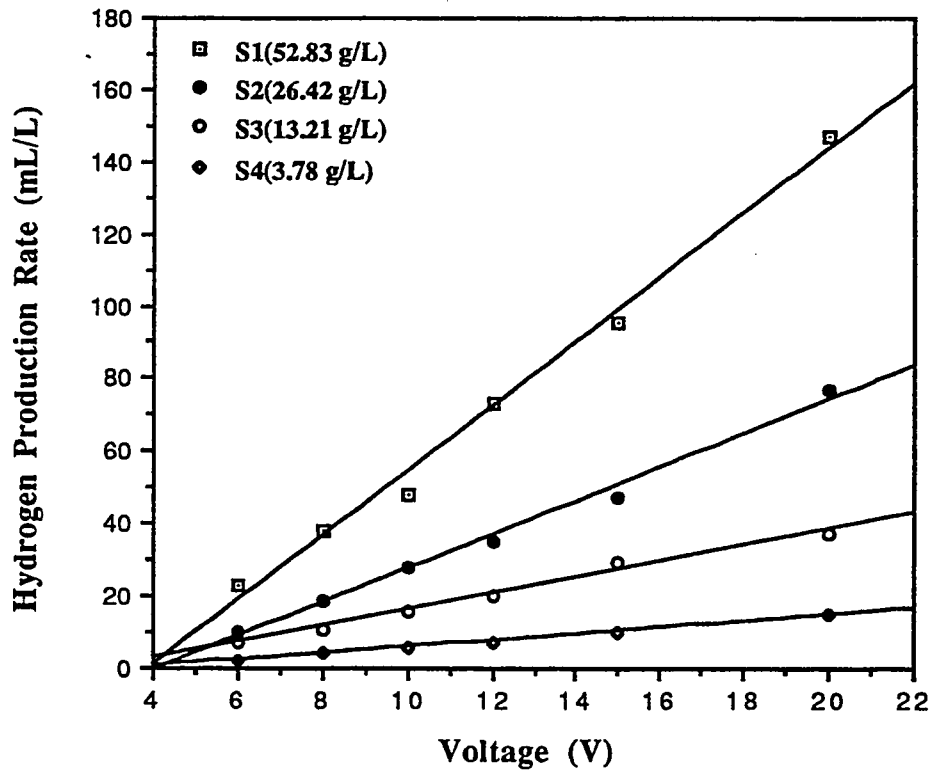


Figure B-1 Hydrogen production rate vs. voltage for NaCl for different concentrations

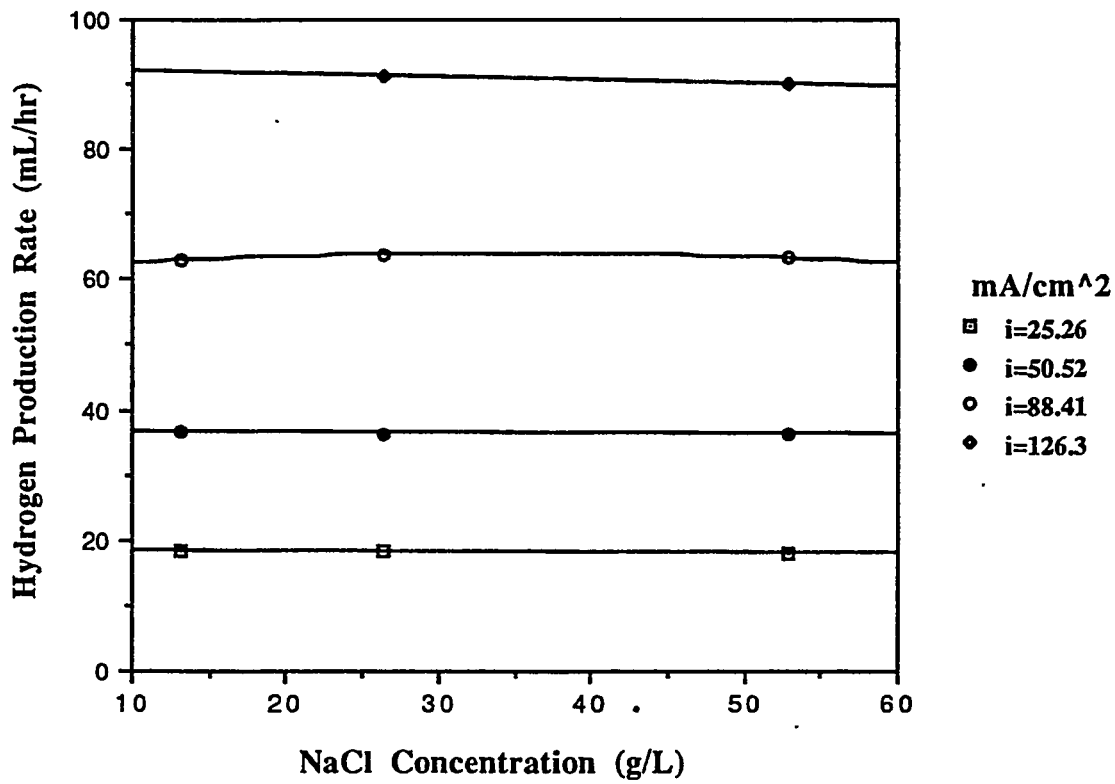


Figure B-2 Hydrogen production rate vs. NaCl concentration at different current densities

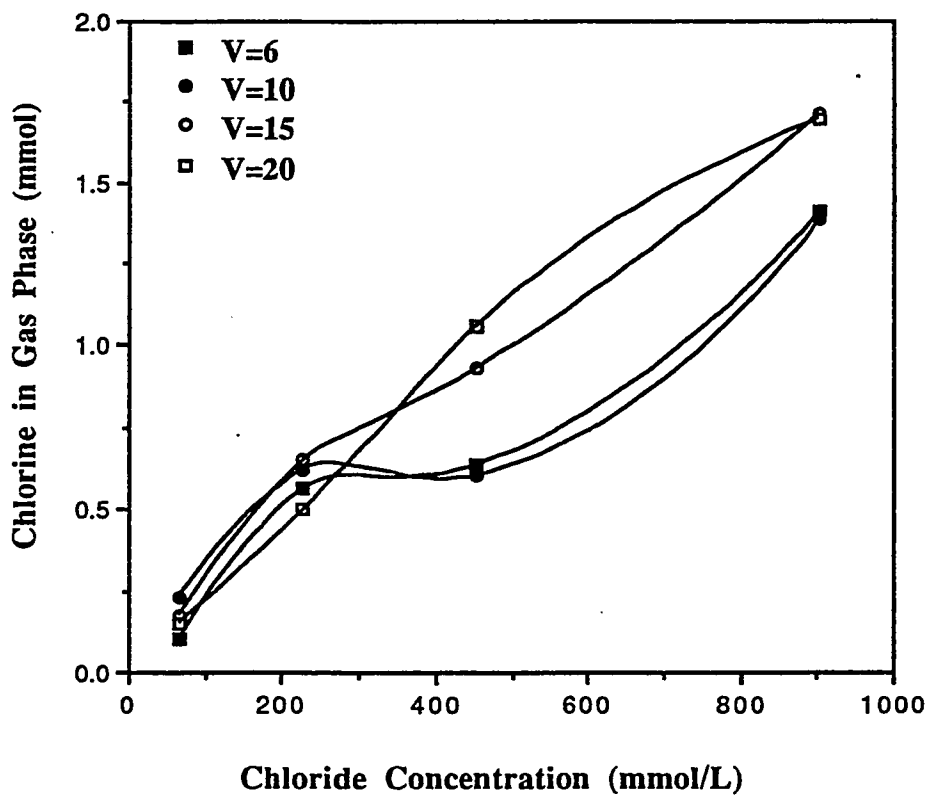


Figure B-3 Chlorine in gas phase vs. chloride concentration for NaCl solutions for different voltages

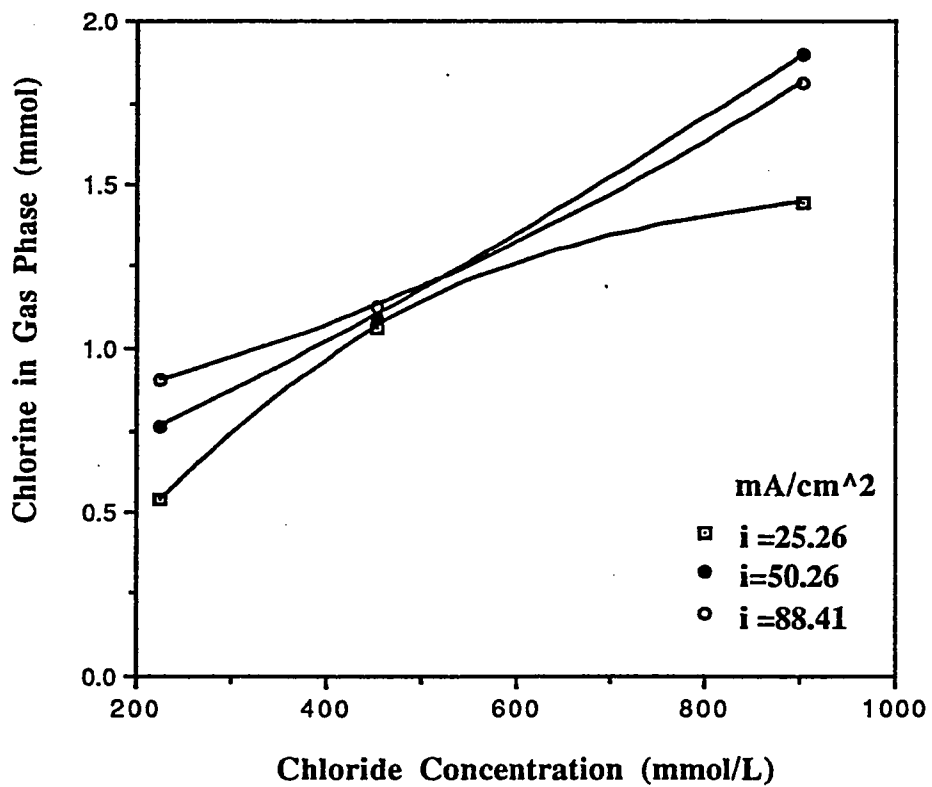


Figure B-4 Chlorine in gas phase vs. chloride concentration for NaCl solutions for different current densities

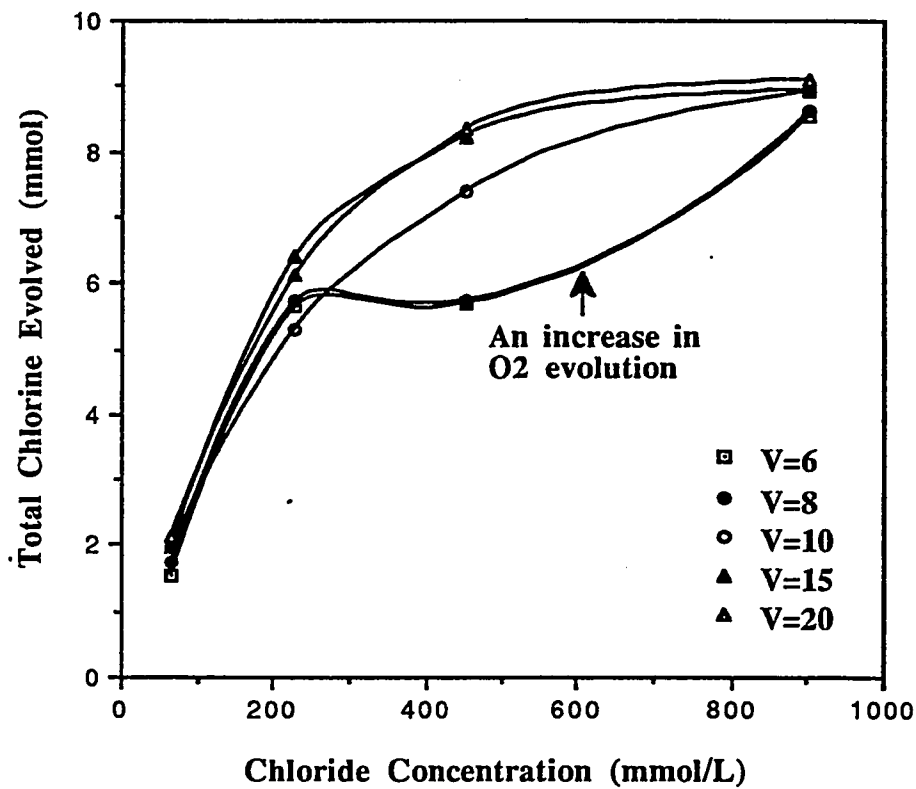


Figure B-5 Total chlorine evolved vs. chloride concentration for NaCl solutions at different voltages

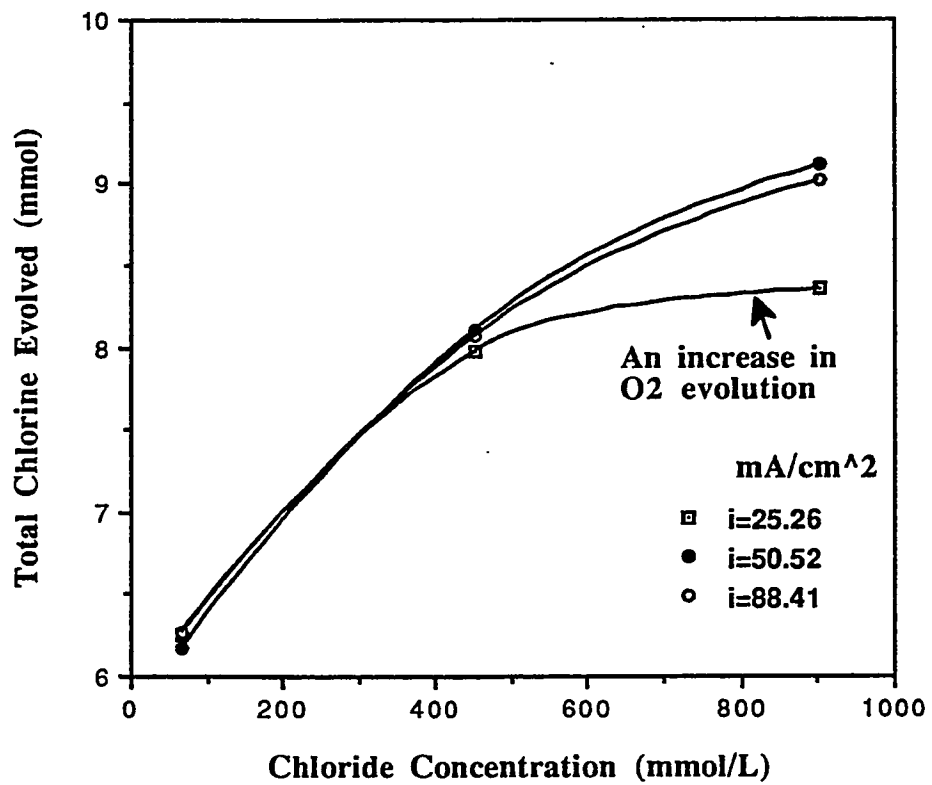


Figure B-6 Total chlorine evolved vs. chloride concentration for NaCl at different current densities

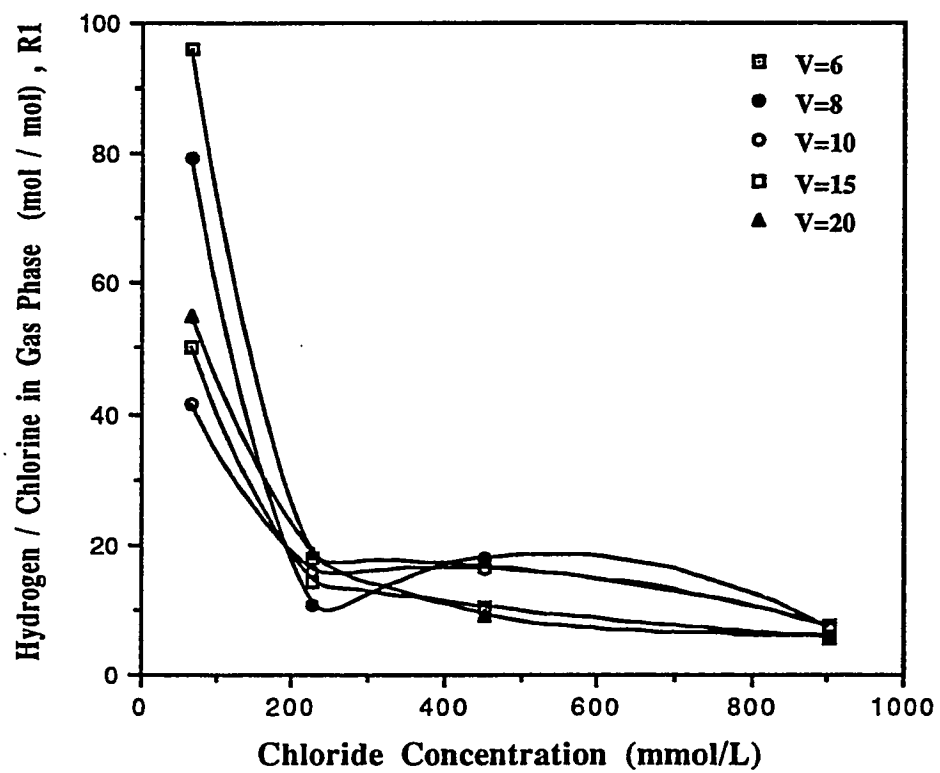


Figure B-7 Hydrogen to chlorine in gas phase vs. chloride concentration for NaCl at different voltages

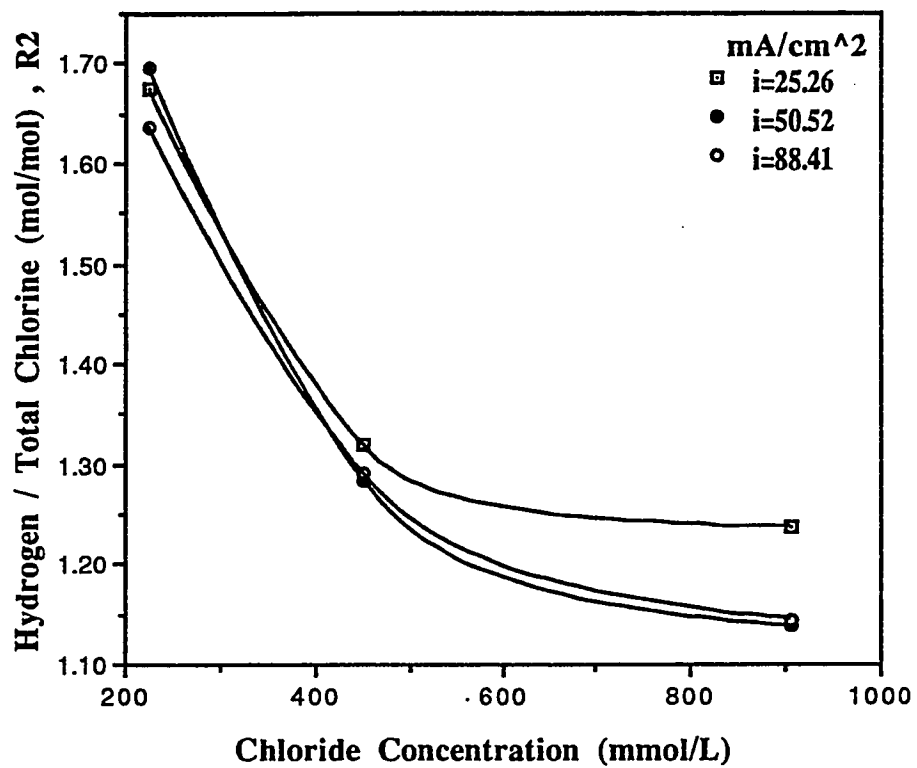


Figure B-8 Hydrogen to total chlorine vs. chloride concentration for NaCl solutions at different current densities

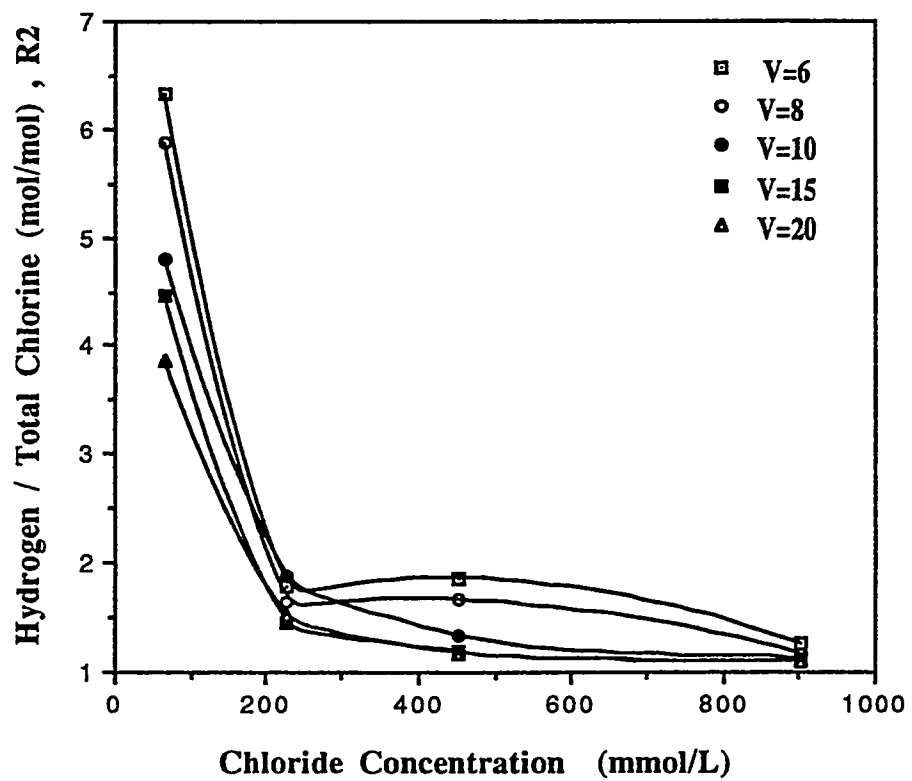


Figure B-9 Hydrogen to total chlorine vs. chloride concentration for NaCl solutions at different voltages

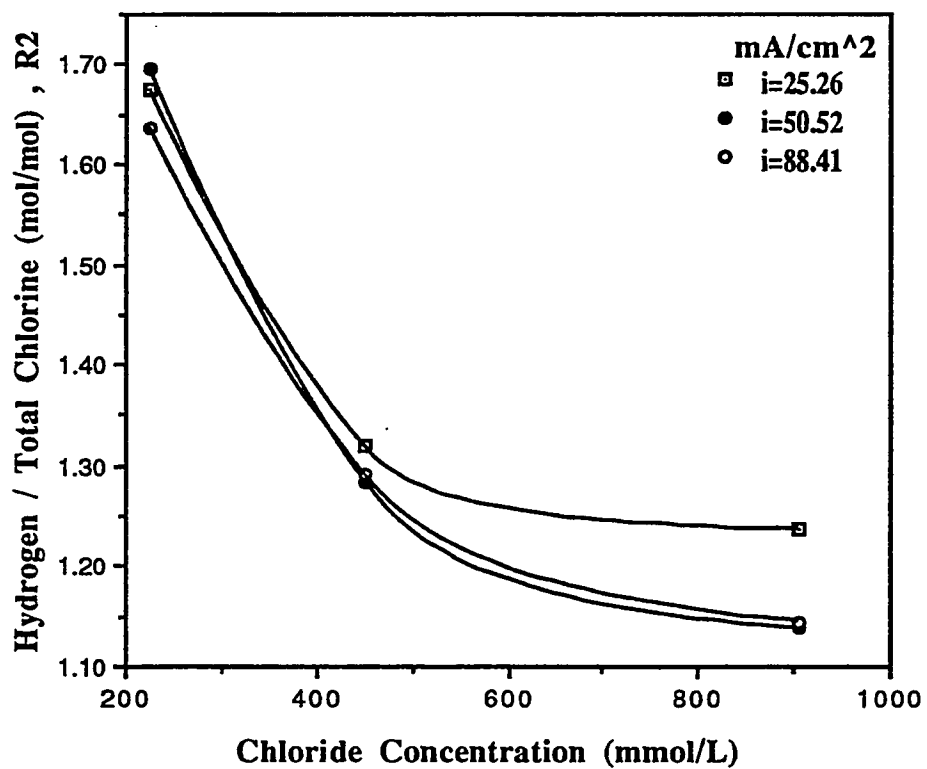


Figure B-10 Hydrogen to total chlorine vs. chloride concentration for NaCl solutions at different current densities

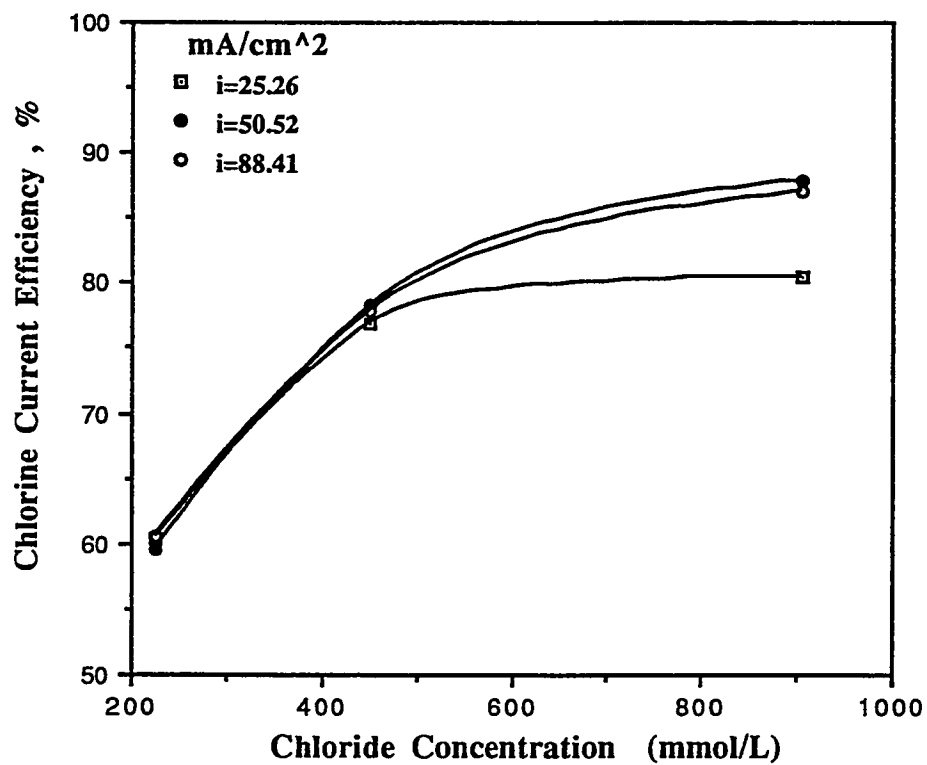


Figure B-11 Variation of chlorine efficiency with chloride concentration for NaCl at different current densities

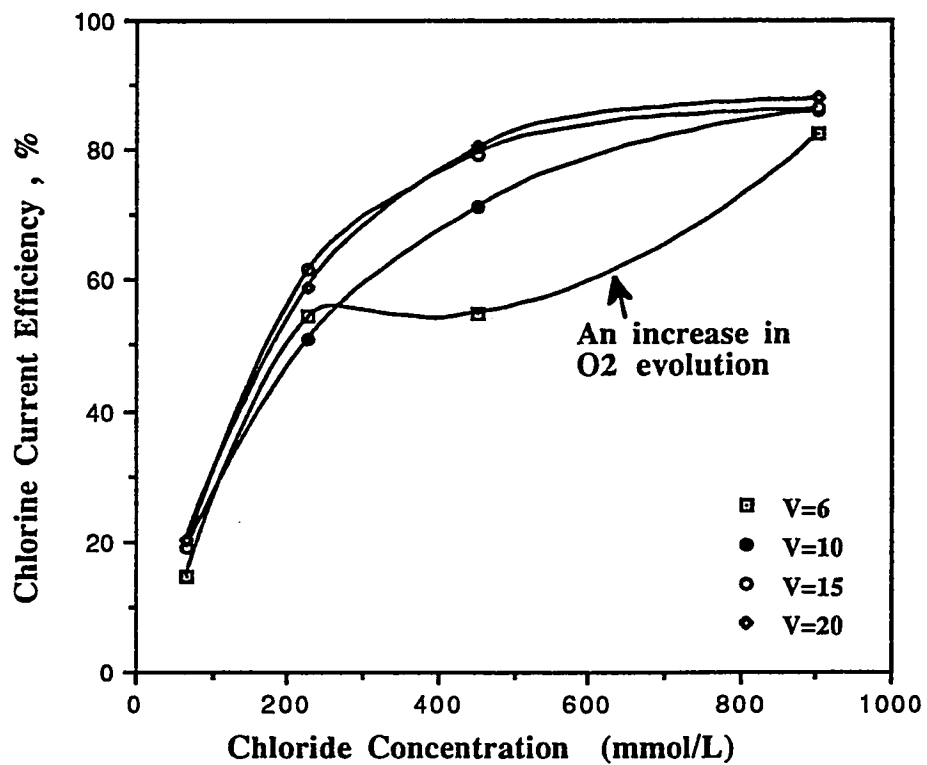


Figure B-12 Variation of chlorine Efficiency with chloride concentration for NaCl solutions at different voltages

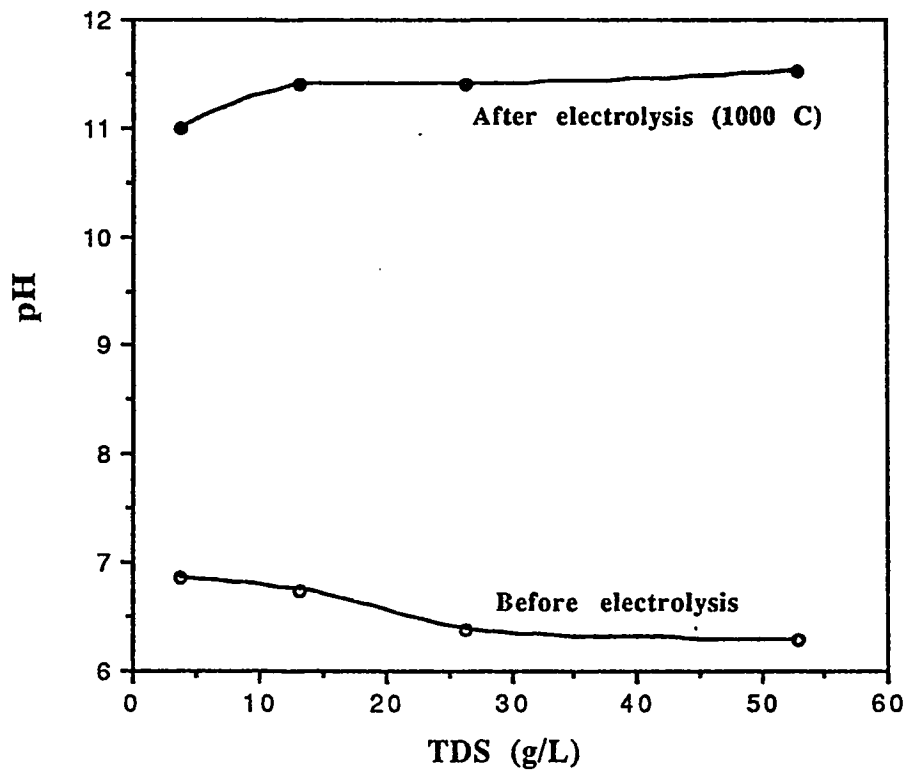


Figure B-13 pH vs. TDS for NaCl solutions before and after electrolysis

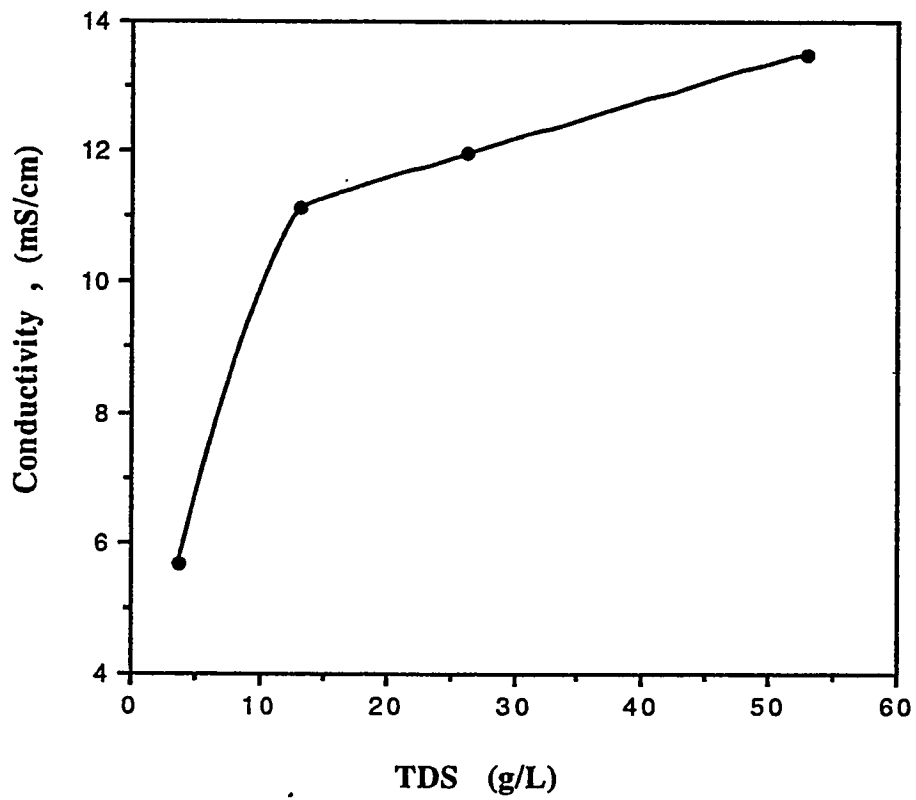


Figure B-14 Conductivity vs. TDS for NaCl solutions

APPENDIX-C
PPOLAROGRAMS

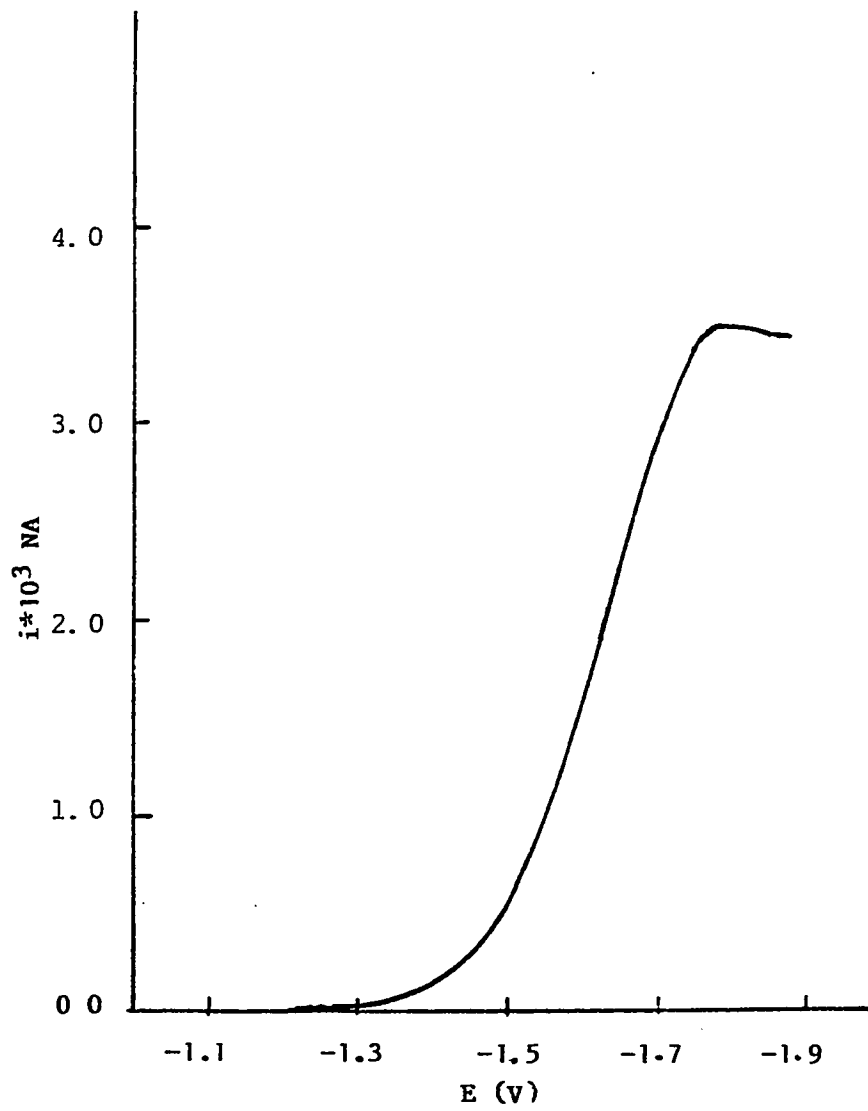


Fig. C-1 Polarogram for deionized water

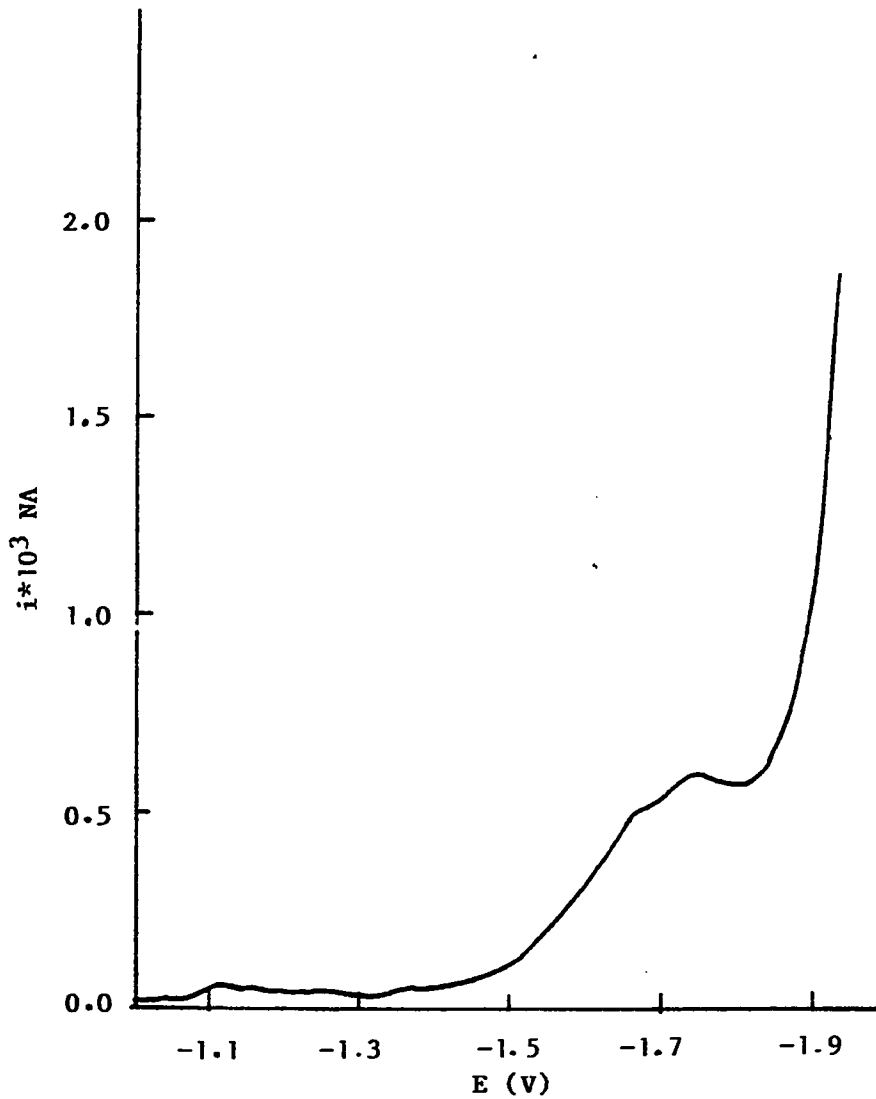


Fig. C-2 Polarogram for NaCl solution (52.83 g/L)

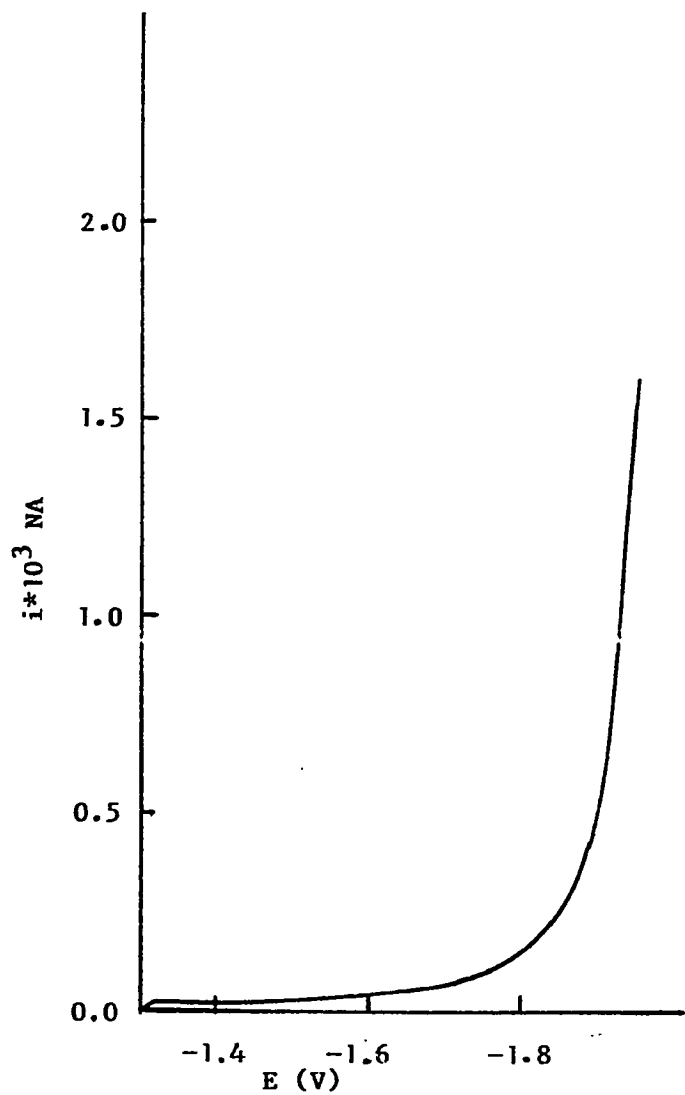


Fig. C-3 Polarogram for NaCl solution (26.42 g/L)

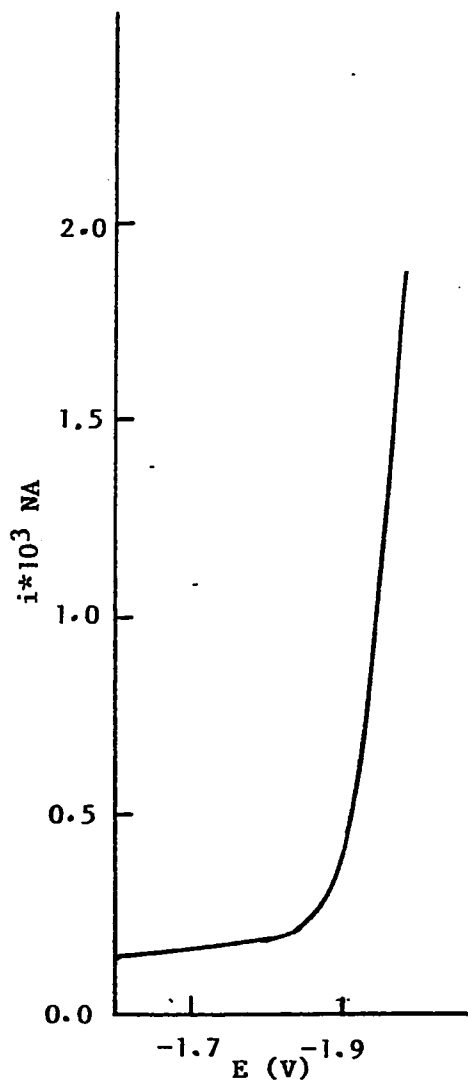


Fig. C-4 Polarogram for NaCl solution (13.21 g/L)

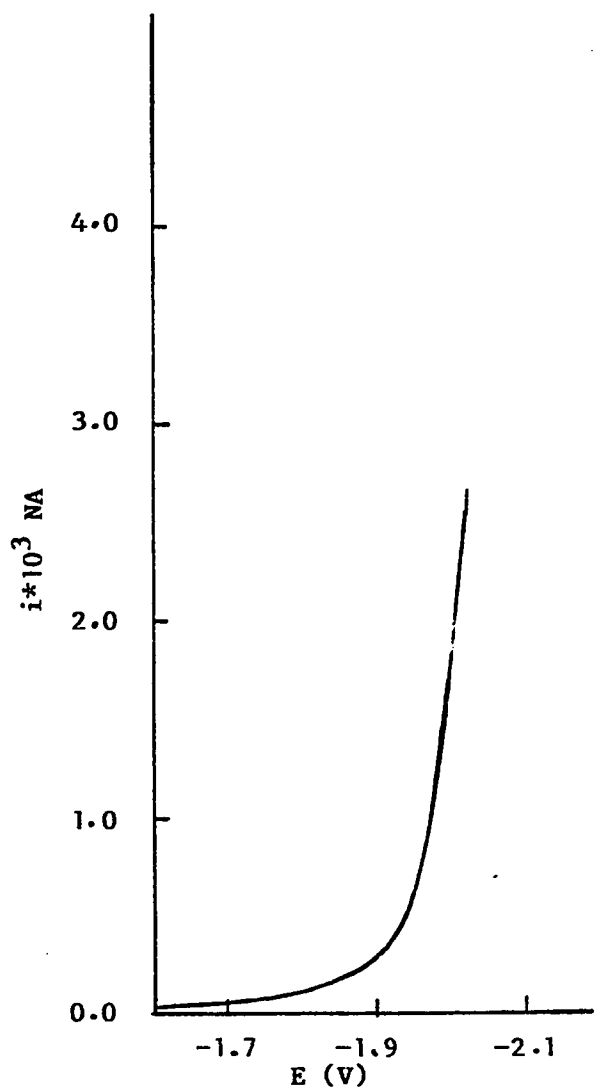


Fig. C-5 Polarogram for NaCl solution (3.78 g/L)

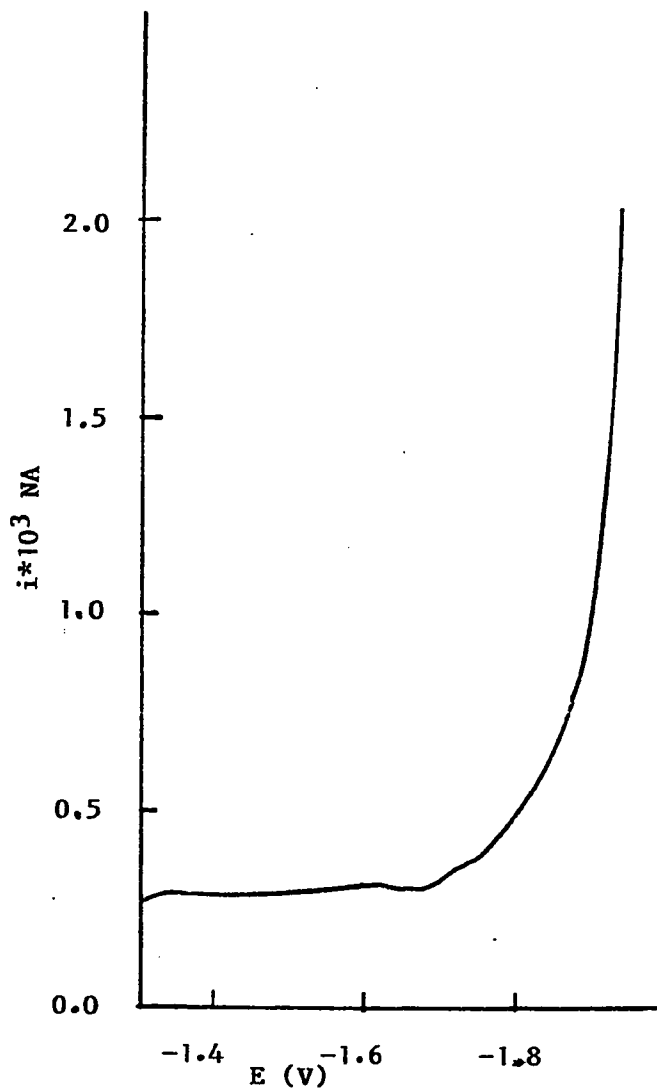


Fig. C-6 Polarogram for synthetic sea water (62.70 g/L)

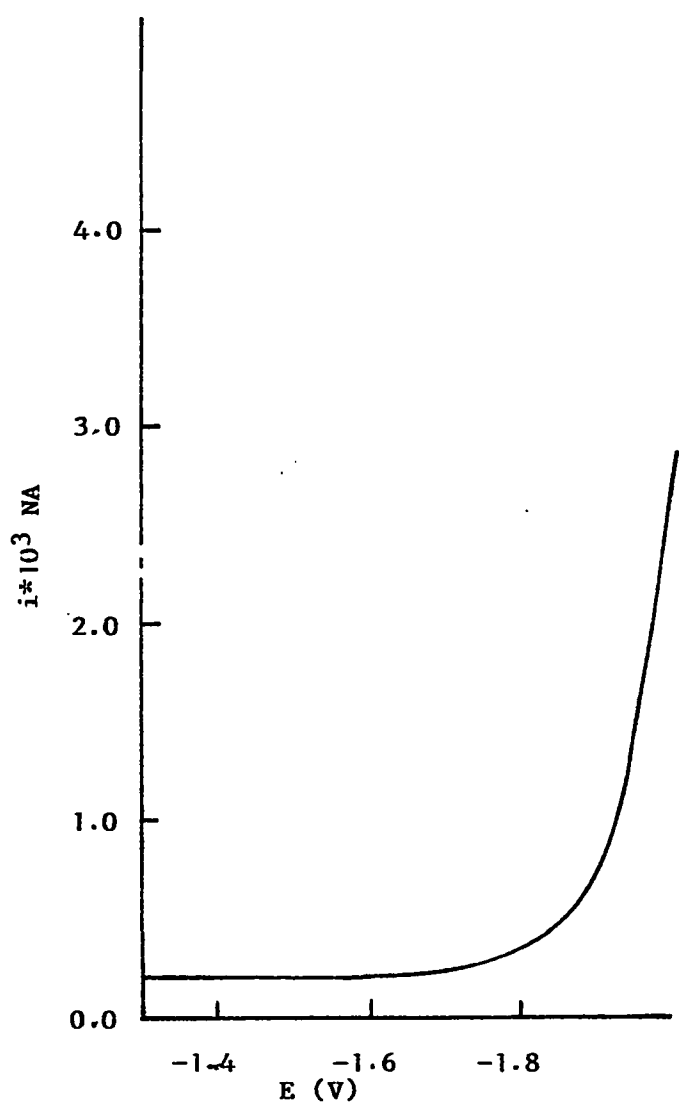


Fig. C-7 Polarogram for synthetic sea water (15.67 g/L)

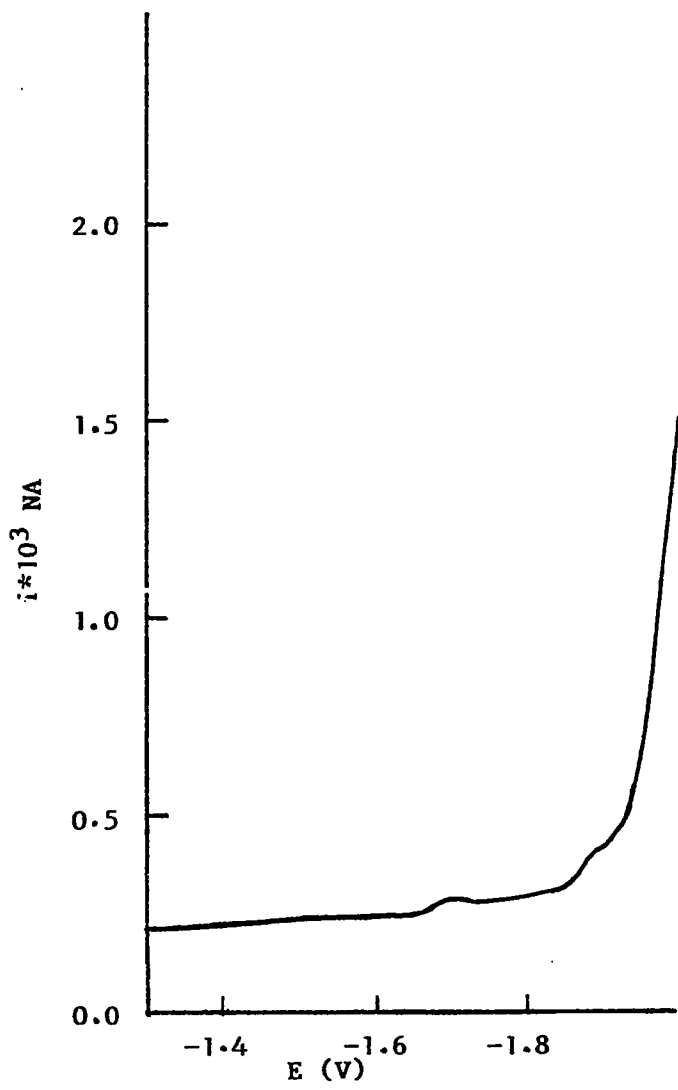


Fig. C-8 Polarogram for synthetic sea water (4.48 g/L)

APPENDIX-D
RAW DATA

Table D-1 Raw data for electrolysis at constant current (1000 C)

HPR=Hydrogen Production Rate

Cl_g=Chlorine in gas phase

CIT=Total chlorine

Current Density, (mA/cm ²)	Parameter Measured	Solutions*									
		S1	S2	S3	S5	S6	S7	SW**			
25.62	HPR (mL/hr)	18.04	18.20	18.32	18.25	18.15	18.24				
50.52		36.30	36.40	36.60	36.73	36.40	36.60	36.00			
69.47				50.64							
88.41		63.16	63.73	62.83	63.80	63.27	63.89	63.07			
101.04											
126.30		90.00	91.22		91.10	91.20	91.20	90.36			
25.62	Cl _g (mmol)	1.445	1.061	0.536	0.396	0.467	0.399	0.319			
37.89		1.895	1.099	0.760	0.234	0.163	0.146	0.329			
50.52				0.666							
69.47		1.809	1.128	0.901	0.260	0.229	0.449	0.122			
88.41											
101.04		2.422	0.941		0.240	0.637	0.351	0.195			
126.30											
25.62		CIT (mmol)	8.350	7.977	6.257	7.769	7.634	7.349	7.402		
37.89	9.112		8.104	6.169	7.998	7.904	7.169	7.981			
50.52				6.244							
69.47		9.015	8.067	6.275	8.124	7.898	7.255	7.908			
88.41											
101.04		9.231	8.209		7.839	7.899	6.854	7.742			
126.30											
25.62		pH	11.43	11.32	11.21	9.32	9.65	9.94	9.55		
37.89	11.53		11.31	11.36	9.35	9.62	10.16	9.60			
50.52				11.26							
69.47		11.55	11.31	11.26	9.35	9.65	10.01	9.52			
88.41											
101.04		11.68	11.38	11.40	9.35	9.71	9.98	9.57			

* The composition was shown in Tables 3.2 and 3.3

** Sea Water

Table D-2 Raw data for electrolysis at constant voltage (1000 C)

Voltage (V)	Parameter Measured	Solutions									
		S1	S2	S3	S4	S5	S6	S7	S8	SW	
5	HPR (mL/hr)	22.96	9.90	7.12	2.4	24.23	14.98	8.541	3.453	12.67	
6		37.65	18.67	10.96	4.28	44.67	24.40	13.17	5.050	17.74	
8		47.81	28.00	16.05	5.91	62.81	31.64	18.10	7.796	33.38	
10		72.89	35.45	20.1	7.51	78.83	43.52	22.86	10.359	40.82	
12		95.40	47.00	29.62	10.30	99.53	53.91	29.19	11.716	57.38	
15		146.87	76.72	37.45	14.95	167.05	80.00	48.20	17.630	79.20	
20									103.74		
6	Clg (mmol)	1.4103	0.6358	0.5638	0.1021	0.853	0.681	0.587	0.535	0.253	
8		1.4433	0.5306	0.8992	0.1281	0.190	0.492	0.560	0.482	0.185	
10		1.3827	0.6036	0.6222	0.2271	0.194	0.237	0.316	0.196	0.236	
12		2.0424	0.3199	0.4640	0.1921	0.442	0.145	0.316	0.284	0.150	
15		1.7158	0.9302	0.6504	0.1761	0.280	0.169	0.191	0.233	0.307	
20		1.6983	1.0591	0.4981	0.1495	1.556	0.303	0.262	0.150	0.976	
6	ClT (mmol)	8.538	5.690	5.670	1.547	7.914	7.239	6.369	4.345	7.683	
8		8.605	5.729	5.748	1.730	8.010	7.814	6.467	4.172	7.827	
10		8.924	7.389	5.302	1.964	7.892	7.616	6.826	3.555	7.710	
12		9.048	6.797	5.347	1.887	7.670	7.949	6.816	4.204	7.759	
15		8.945	8.237	6.396	1.976	8.580	7.989	7.030	3.272	8.059	
20		9.106	8.333	6.121	2.124	8.082	8.558	7.190	8.112	8.551	

Table D-3 Raw data for total chlorine and chlorine in gas phase for sea water

Current Density (mA/cm²)	Parameter Measured	Sea Water	
		500 C	1500 C
37.89	Cl_g (mmol)	0.033	1.309
50.52		0.036	1.374
88.41		0.050	0.373
101.04		0.024	0.841
126.3		0.039	2.117
37.89	CIT (mmol)	4.182	11.783
50.52		4.319	11.737
88.41		4.288	11.349
101.04		4.363	11.393
126.3		4.021	11.777

Table D-4 Raw data for synthetic and natural sea water precipitates (mg)

Current Density (mA/cm ²)	Synthetic sea water (1000 C)			Sea water		
	S5	S6	S7	500 C	1000 C	1500 C
25.26	1.750	1.029	0.650			
50.52				0.418	0.933	1.212
88.41	1.053	0.608	0.326	0.184	0.560	0.39
101.04	0.879	0.632	0.338	0.036	0.657	0.694
126.3				0.061	0.735	0.838

Table D-5 Raw data for the solar run on 19/11/91

Day Hours	Temp. (°C)	Radiation (Whr/m²)	Hydrogen Produced (mL)	Current Density (mA/cm²)
9:00	23.8	535		
9:30			0	59.93
10:00	25.0	712	21.4	58.54
10:30			41.7	57.59
11:00	27.2	809	62.0	56.27
11:30			81.6	55.76
12:00	28.5	816	100.3	55.84
12:30			119.0	55.95
13:00	29.1	780	137.7	54.75
13:30			155.7	55.32
14:00	28.7	673	174.0	55.32
14:30			193.5	55.95
15:00	27.7	484	211.1	56.08
15:30			228.7	55.84