

## THE MANUFACTURE OF PERCHLORATE BY DIRECT METHOD USING GRAPHITE SUBSTRATE LEAD DIOXIDE (GSLD) ANODE

**Ahmed D. Wiheeb**

Chem. Eng. Dept., College of Eng., University of Tikrit  
(Received:25/1/2009 ; Accepted:12/4/2009)

**ABSTRACT** - Sodium perchlorate has been prepared electrochemically from sodium chloride solutions in one step by passing a direct current through the solution , in the presence of certain addition agents (like sodium fluoride). A laboratory electrolytic cell has been designed to obtain experimental results for the preparation of sodium perchlorate. A solution of sodium chloride (290 g/l ) and sodium fluoride (2 g/l ) is electrolyzed in a batch wise. A stainless steel cathode and Graphite substrate lead dioxide (GSLD) anode are satisfactory . The influence of anodic current density , temperature ,and pH of electrolyte on current efficiency of sodium perchlorate formation were studied. The current efficiency of about 68% was obtained by using (GSLD) anode.

**Keywords:** Perchlorate , Lead dioxide anode , GSLD anode , Direct oxidation of sodium chloride.

---

### 1. INTRODUCTION

Perchlorate is an inorganic chemical compound consisting of chlorine bonded to four oxygen atoms ( $\text{ClO}_4^-$ ) and is usually found as the anion component of a salt most often associated with either of these common cations: ammonium ( $\text{NH}_4^+$ ), sodium ( $\text{Na}^+$ ), lithium ( $\text{Li}^+$ ) or potassium ( $\text{K}^+$ ). They have been used as a medicine for more than 50 years to treat thyroid gland disorders<sup>(1)</sup>. They are also used as an oxidizer in rocket fuel and can be found in airbags,

fireworks, and Chilean fertilizers<sup>(2)</sup>. Both potassium perchlorate (KClO<sub>4</sub>) and ammonium perchlorate (NH<sub>4</sub>ClO<sub>4</sub>) are used extensively within the pyrotechnics industry, whereas ammonium perchlorate is a component of solid rocket fuel. Lithium perchlorate, which decomposes exothermically to give oxygen, is used in oxygen "candles" on spacecraft, submarines and in other esoteric situations where a reliable backup or supplementary oxygen supply is needed. Most perchlorate salts are soluble in water<sup>(1,3)</sup>. Perchlorates occurs naturally in soils, even foods, and being found with increasing frequency in water<sup>[3]</sup>. It can be prepared both chemically and electrochemically. The advent of commercially produced pure perchloric acid directly from hypochlorous acid means that several metal perchlorates can be prepared by the reaction of perchloric acid and a corresponding metal oxide, hydroxide, or carbonate but this method is not economical since the price of perchloric acid is about twice as high as the present market price of ammonium perchlorate. Perchlorates have been produced electrochemically by a three-steps process: (1) electrochemical production of sodium chlorate; (2) electrochemical oxidation of sodium chlorate to sodium perchlorate; and (3) metathesis of sodium perchlorate to other metal perchlorates<sup>(4)</sup>. Because of the high solubility of sodium perchlorate, its isolation is avoided when it is used as an intermediate to produce other perchlorates. The manufacture of other perchlorate salts takes advantage of their lower solubilities. Potassium perchlorate is prepared by the double decomposition reaction of sodium perchlorate and potassium chloride.



The electrochemical method is convenient to use if you have a perchlorate cell with the right anodes already, since then making perchlorate is simply a matter of operating the cell for a bit longer.

## 2. THEORY

The methods so far in vogue for the electrolytic preparation of perchlorates involve two steps; the first stage being the electrochemical oxidation of sodium chloride to sodium chlorate in an electrolytic cell according to the following anodic reaction<sup>(5)</sup>:



The kinds of anodes used in this electrolysis stage are graphite<sup>(6)</sup> or magnetite<sup>(7)</sup> or metal oxide-coated titanium electrodes (like DSA)<sup>(8)</sup> or lead dioxide anodes<sup>(9)</sup>. The second

stage being the electrochemical oxidation of sodium chlorate which is carried out at the anode in an electrolytic cell according to the following reaction:



The standard potential for the anodic reaction is 1.19 V, close to that of 1.228 V for water oxidation. In order to minimize the oxygen production from water oxidation, the cell is operated at a high potential that requires either platinum<sup>(10)</sup> or lead dioxide anodes<sup>(11,12)</sup>. Various mechanisms have been proposed for the formation of perchlorates at the anode, including the discharge of chlorate ion to chlorate radical<sup>(13)</sup>, the formation of active oxygen and subsequent formation of perchlorate, and the mass-transfer-controlled reaction of chlorate with adsorbed oxygen at the anode<sup>(14)</sup>. Sodium dichromate is added to the electrolyte in platinum anode cells to inhibit the reduction of perchlorates at the cathode. Sodium fluoride is used in the lead dioxide anode cells to improve current efficiency<sup>(4)</sup>.

This conventional process has various drawbacks, such as: (i) that in between the two stages the solutions have been processed to isolate the chlorate and recover the unconverted chloride; (ii) that graphite gets disintegrated to a considerable extent and magnetite to lesser extent when used in the production of chlorates; and (iii) that there is an inevitable loss of platinum due to corrosion in the perchlorate cell. With a view to avoiding the intermediate step of the processing of the liquor after the said first stage of the conventional process, it has been proposed that the effluent from the chlorate cell should be treated under different electrolytic conditions from those in which the sodium chloride solution was treated in the chlorate cell during the first stage of the process. But this proposed process also is a two stage process and the processing of the effluent from the chlorate cell introduces complications in the method<sup>(15)</sup>. The main object of this research has to improve method which will obviate the drawbacks of known methods, and whereby the perchlorates may be prepared directly from sodium chloride in a single step of electrolytic oxidation, the conditions of electrolysis being maintained constant at predetermined levels throughout the period. Another object of this research is to avoid the use of graphite, magnetite or platinum as the anode. With these and other objects in view, this research broadly consists of a process of preparing sodium perchlorate directly from sodium chloride in a single step of electrolytic oxidation, which consists in passing a direct current through a bath of sodium chloride solution containing fluoride ions. The anode used in this process is graphite substrate lead dioxide (GSLD). The lead dioxide deposited structure was 98%β- PbO<sub>2</sub> and 2% α- PbO<sub>2</sub> and the thickness of lead dioxide layer was ( 1mm. ± 0.05 mm.)

### 3. CHOOSING ELECTRODES MATERIALS

The cathode materials which are suitable used for perchlorate cells were stainless steel like in chlorate cells, mild steel, copper and brass also work, they may cause problems with copper contamination when they erode. Anode materials for perchlorate cells should have a high oxygen over potential. It suffices to say that if the oxygen over potential at a certain anode material is not high enough oxygen will be evolved instead of chlorate oxidized to perchlorate. No perchlorate will be formed, and the anode material is usually attacked comparatively quickly. This holds also for chlorate cells, but the problem is less severe there since lower potentials are involved. Anode materials suitable for perchlorate synthesis are listed below<sup>(11,16)</sup>.

#### 3.1. *Platinum*

The obvious disadvantage of platinum is its high price. However, it corrodes only at a very slow rate and therefore provides almost an ideal anode material. High efficiency can be reached with platinum and processing of the electrolyte is greatly simplified due to the absence of insoluble anode erosion products<sup>(10,16)</sup>.

#### 3.2. *Lead dioxide*

Lead dioxide provides an economical alternative to platinum. Efficiency of lead dioxide anode based cells is usually slightly lower than that of platinum based cells, but the difference is small. Lead dioxide anodes are not easily bought and must be made. This takes some work and effort, but the anodes are cheap, fairly resistant to corrosion even at higher temperatures<sup>(11,17)</sup>.

#### 3.3. *DSA*

DSA stands for Dimensionally Stable Anode. This is the common term used to refer to anodes consisting of a layer of noble metal oxides (usually RuO<sub>2</sub> and TiO<sub>2</sub>) coated onto a substrate, usually titanium. This type of anode is finding increased use in industrial cells because of its comparatively low cost when compared to platinum and its resistance to corrosion. The chemicals required to manufacture these anodes are expensive and difficult to handle. However, if the chemicals can be obtained and suitable equipment is available, the procedure to make the anode seems fairly straightforward and may be an option<sup>(8, 16)</sup>.

### **3.4. Magnetite**

This material has found use in industry in the past, but is rarely used nowadays due to its relatively high corrosion rate and low efficiency for perchlorate manufacture. The anodes are made by melting and casting  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$  into the required anode shapes<sup>(7, 16)</sup>.

## **4. EXPERIMENTAL WORK**

### **4.1. Electrolytic Cell Construction**

The electrolytic cell assemble consisted of a 250 ml. tall-form beaker with a cell cover made of " plastic " with holes to introduce anode , cathode , and thermocouple. The cell was placed in an outer water bath to heat the electrolyte to the desired temperature. A steel cooling coil was passed a round the cell for cooling it. The liquid passing through the coil is water which is coming from cold water container by pumping it to the coil. A contactor was connected with the pump and thermocouple to control the temperature of the cell through the experiment running. Graphite Substrate Lead Dioxide (GSLD) anode prepared by depositing lead dioxide on graphite rod ( 10 cm. length and 1 cm. diameter ) from lead nitrate bath ( 350 g/L ), at temperature range (60 to 65 °C ) and pH range (4 to 4.5)<sup>(11)</sup>. The lead dioxide deposited on graphite rod until the diameter of the rod become 1.2 cm. A rotating technique for cylindrical rod was used. Two bent, perforated stainless steel plates (5.5 x 8.5 cm.) acted as cathodes. Anode – cathode spacing was 1 cm. see fig. (1).

### **4.2. Preparing the Electrolyte**

The electrolyte was prepared by dissolving about 290 g. of sodium chloride in distilled water to give 1000 ml of solution. The exact initial chloride content of this solution was determined by the iodometric titration method. The solution pH was adjusted to a suitable value using dilute NaOH solution.

### **4.3. Experimental Procedure**

The electrolytic cell first filled with 200 ml. of electrolyte for each experiment, and then it was placed in water bath and heated the electrolyte to the desired temperature. The anode, cathode, and thermocouple were dipped in the electrolyte through the holes in the cell cover at a desirable height. The power supply was switched on to provide a constant current. Also the pump was operated to adjust the temperature of the electrolyte. At the end of the theoretical

time to converted sodium chloride to sodium chlorate , (2 g/l) of sodium fluoride was added to the electrolytic solution. The pH of the electrolyte was adjusted to a suitable value by adding small amount of dilute hydrochloric acid from time to time. Some water adding from time to time to make up for what has evaporated. A known amount of electrolyte (5 ml.) piped out for analysis by iodometric titration method <sup>(18)</sup> , after full theoretical time for the chloride to chlorate conversion and the chlorate to perchlorate conversion , then the current efficiency is calculated.

## **5. RUSULTS AND DISCUSSION**

The manufacture process of sodium perchlorate by direct method from sodium chloride in one electrolytic cell using graphite substrate lead dioxide (GSLD) as anode influenced by many variables such as anode current density, temperature, and pH of electrolyte. The influence of each variable on current efficiency can be study to find the optimum operating conditions for manufacturing of sodium perchlorate by direct method :

### **5.1. Influence of Anode Current Density**

The influence of anode current density on current efficiency was studied in the range of 15 to 30 Amp/dm<sup>2</sup> .The result were explained in figures (2) to (4) .It can be seen that the relation between anode current density and current efficiency at different values of temperature and pH of electrolyte have the same behavior. In fig.(2) it is observed that at anodic current density less than 15 Amp/dm<sup>2</sup> the current efficiency less than (34%) while at anodic current density higher than 15 Amp/dm<sup>2</sup> the current efficiency increases until it reaches a maximum at (22 to 25 Amp/dm<sup>2</sup> ) .After this the current efficiency decreases again. This results can be interpreted as that increasing anode current density could in theory increase the reaction rate due to increasing anode potential for chlorate and perchlorate formation , were it not that the anode erosion increases with increasing current density. This interpreted the increasing in current efficiency with increasing anode current density up to the optimum value (22 to 25 Amp/dm<sup>2</sup> ). After that the current efficiency decreases with increasing anode current density this may be due to formation another materials such that hypochlorite , chlorine or chloric acid , or due to decomposition perchlorate ion.

### **5.2. Influence of Temperature**

Figures (5) to (7) shows the influence of electrolyte temperature on current efficiency for different anode current density at constant pH of electrolyte. The temperature increase has a positive effect on current efficiency , since increasing temperature will also increase the rate of electrochemical reaction to produce perchlorate due to activation energy effects and

decreases the viscosity in the solution, which leads to an increase in the ionic mobility of  $\text{Cl}^-$  and  $\text{ClO}_3^-$  to the anode surface. On the other hand the increase in temperature above  $45^\circ\text{C}$  has a negative effect on current efficiency because of increases the rate of decomposition of chloric acid due to the activation energy effects. The current efficiency decreases above  $45^\circ\text{C}$  may be due to another side reaction which consumed current and caused current efficiency to decrease or it may be interpreted as at increasing cell temperature the cell voltage is reduced and this reduced current efficiency.

### **5.3. Influence of Electrolyte pH**

The influence of electrolyte pH on the current efficiency was studied in the range (5 to 9). The results are shown in figures (8) and (9). It is observed that we can manufacture sodium perchlorate from sodium chloride in one electrolytic cell with optimum pH value in the range of (6 to 7) slightly acidic solution, to give current efficiency of 68%. In very acidic solutions when hypochlorous species decompose and tend to negligible concentration, chlorine evolution approaches its maximal current yield, chlorate current efficiency takes small values and the whole cell operates as a chlorine producing unit. On the contrary in alkaline solutions, hypochlorous acid approaches zero concentration and all active chlorine builds up its concentration and exist in the form of hypochlorite ions. This reduces chemical conversion of available chlorine to negligible rates so that the final product represents chlorate production takes place from total anodic oxidation only.

## **6. CONCLUSIONS**

Depending on the results of this investigation, the following conclusions can be drawn

1. The (GSLD) anode is considered as the best alternative anode to graphite which is used in the preparation of sodium chlorate from sodium chloride and also used in the preparation of sodium perchlorate from sodium chlorate. It is inert and insoluble in the electrolysis process, whereas the graphite anode is eroded during the electrolysis process forms mud, then the product needs filtration.
2. The current efficiency in the manufacture process of sodium perchlorate from sodium chloride by direct method in one electrolytic cell provided with (GSLD) anode is (about 68%) when using anode current density in the range of 23 to 25  $\text{Amp}/\text{dm}^2$ .
3. The highest current efficiency is attained at temperature range of  $43$  to  $45^\circ\text{C}$ .
4. The optimum pH of electrolyte which gives high current efficiency is in the range of 6.5 to 7 (slightly acid to normal) >

## REFERENCES

1. from Wikipedia, the free encyclopedia , <http://en.wikipedia.org/wiki/Perchlorate>.
2. " Draft Toxicological Profile for Perchlorates, Agency for Toxic Substances and Disease Registry ", U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, September, 2005 .
3. Perchorate " from , the Learning and Developmental Disabilities Initiative February 2007.
4. Kirk-Othmer, Encyclopedia of Chemical Technology , 4<sup>rd</sup> edition , Wiley Interscience Pub .New York , Vol.18 , P.67, 1992.
5. Milan M. Jaksic , J. Electrochem. Soc. , Vol.121 , No.1 , P.70-79 , January 1974 .
6. Groggins P. H., Pitman A. L., McLare J. and Davis F. H., Chem. Met. Eng., 44, 302 (1937).
7. B.I.O.S. Final report No. 1200.
8. Talib A. " Study The Factors Affecting The Cells Of Sodium Chlorate Production " , M.Sc. , Thesis , University of Baghdad , 2002 .
9. Udupa H. V. K. , Indian Journal Tech., 9, 257 (1971).
10. Udupa H. V. K. , Indian Chem. Eng., 9, 28 (1967).
11. Al-Kubaisy A.D., " Study The Factors Affecting The Cells Of Sodium Perchlorate Production " , M.Sc. , Thesis , University of Baghdad , 2002 .
12. Narasimham K. C., Sundararajan S., and Udupa H. V. K., J. Electrochem. Soc., Vol. 108, P- 798 (1961).
13. Sugino K. and Aoyagi , J. Electrochem. Soc. ,Vol. 103 , P. 166 (1956).
14. U. S. Pat. 3,475,301 ( Oct. 28, 1969 ).
15. U. S. Pat. 3,493,478 ( Feb. 3, 1970 ).
16. Schumacher, J.C., "Perchlorates", New York, Reinhold Publishing Corp., 1960.
17. U. S. Pat. 4,038,170 ( July, 26, 1977 ).
18. Vogel, I., Quantitative Inorganing Analysis, 3<sup>rd</sup> Edition, Longmans (London) , 1961.

THE MANUFACTURE OF PERCHLORATE BY DIRECT METHOD USING GRAPHITE  
SUBSTRATE LEAD DIOXIDE (GSLD) ANODE

---

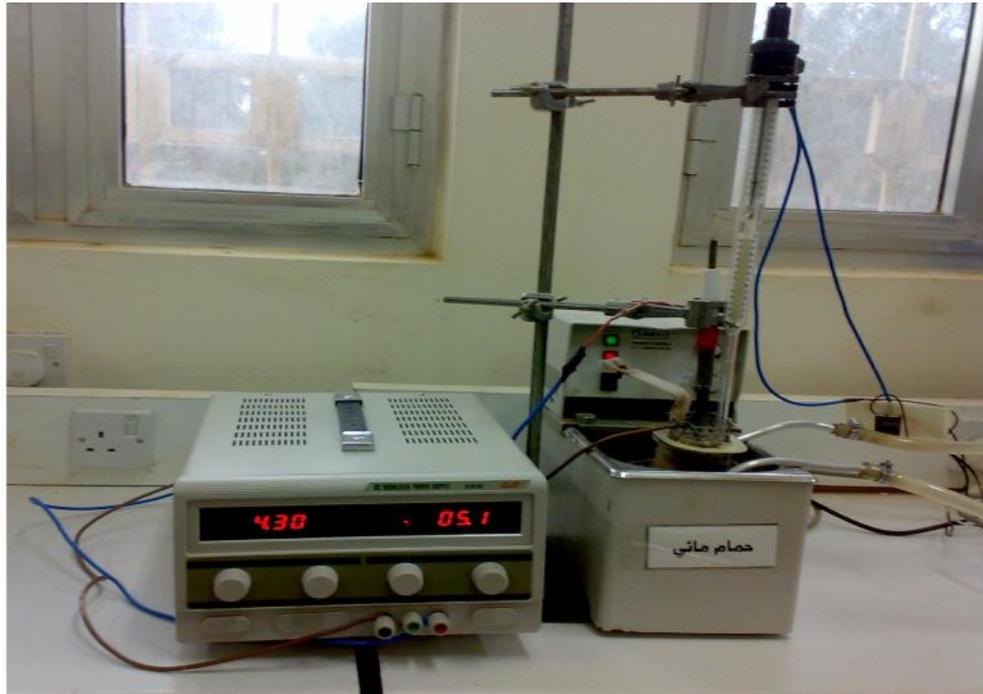


Fig. (1): The Electrochemical system for the manufacture of sodium perchlorate

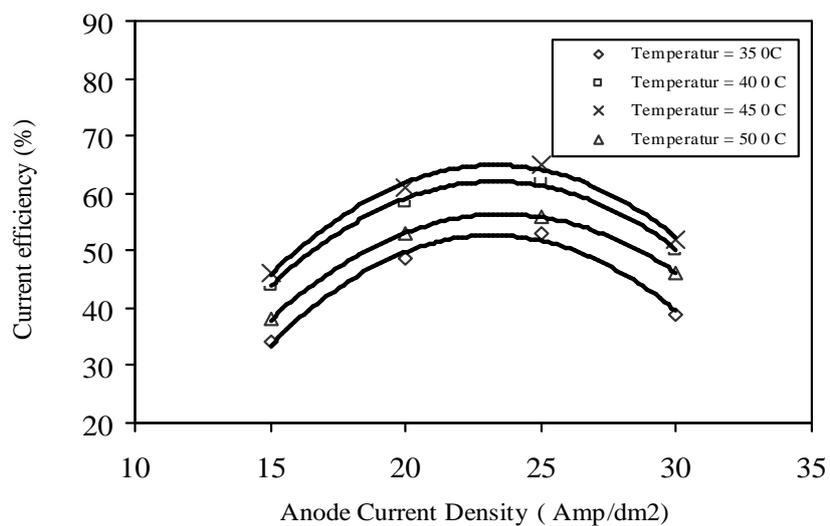
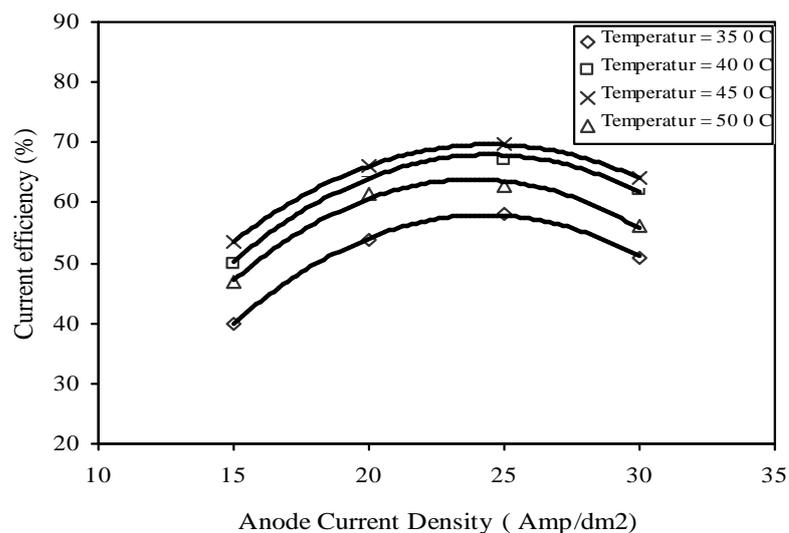
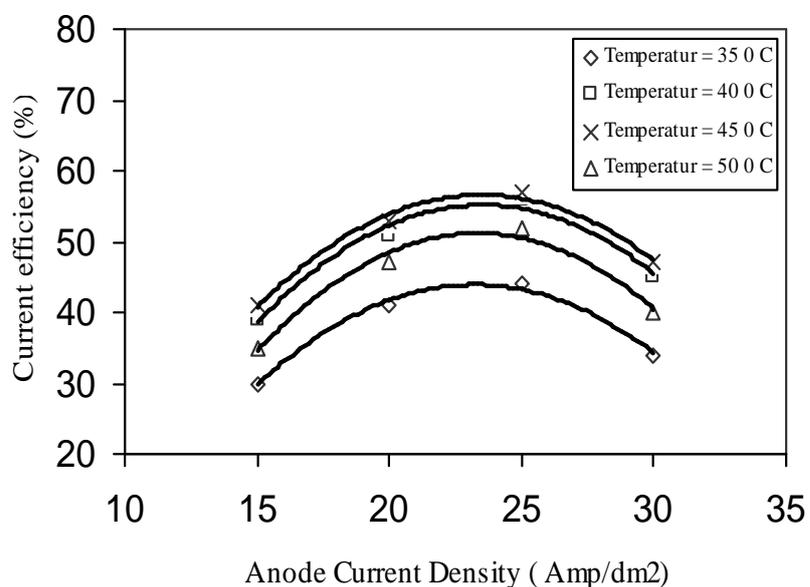


Fig.(2) : Variation of Current Efficiency with Anode Current

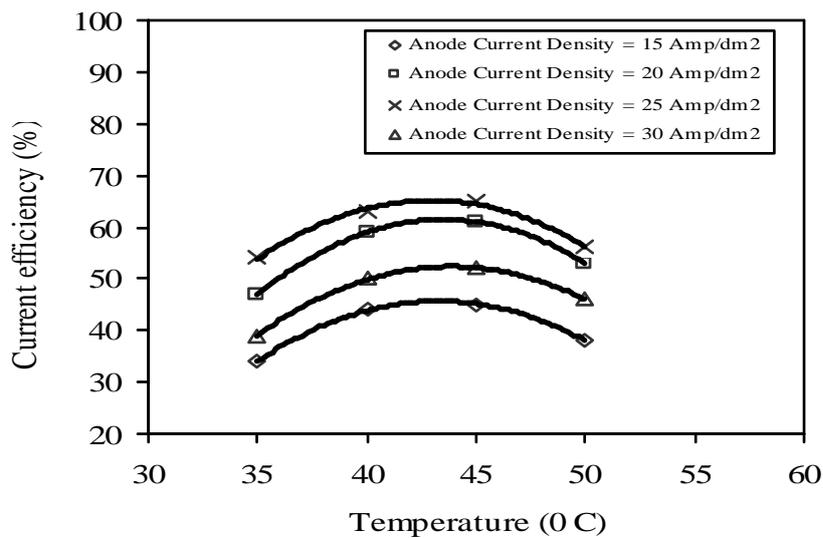
**Fig. (2):** Variation of Current Efficiency with Anode Current Density as a function of Temperature at pH = 5



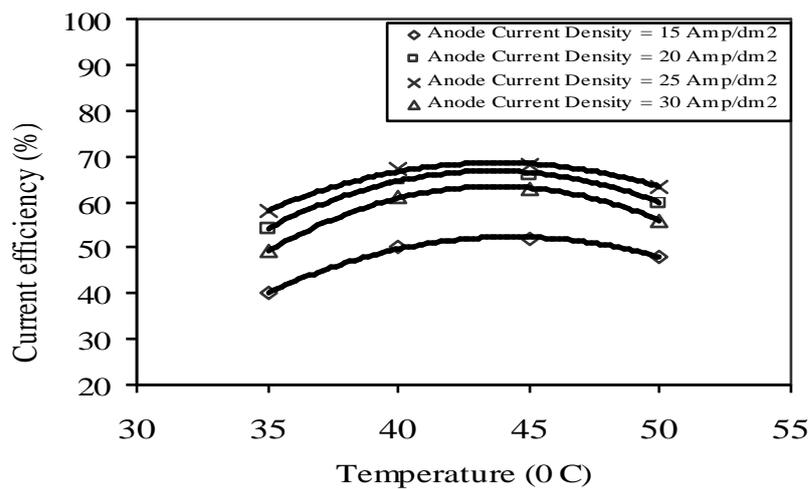
**Fig. (3):** Variation of Current Efficiency with Anode Current Density as a function of Temperature at pH = 7



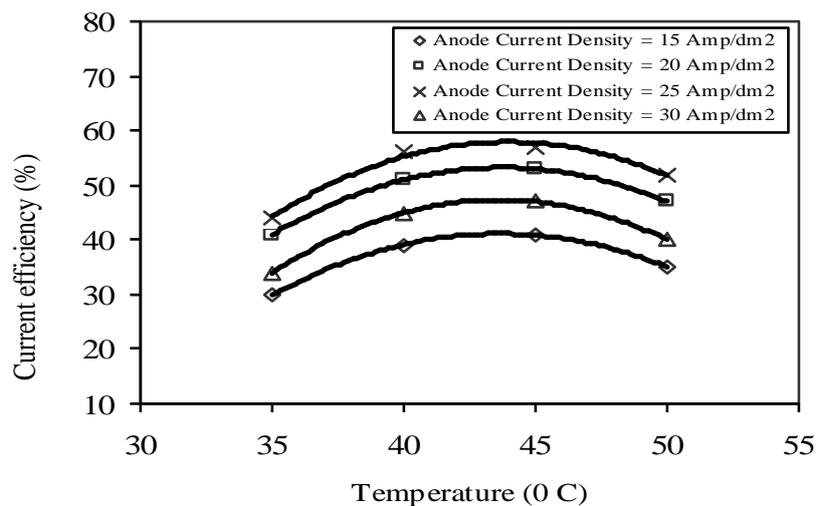
**Fig. (4):** Variation of Current Efficiency with Anode Current Density as a function of Temperature at pH = 9



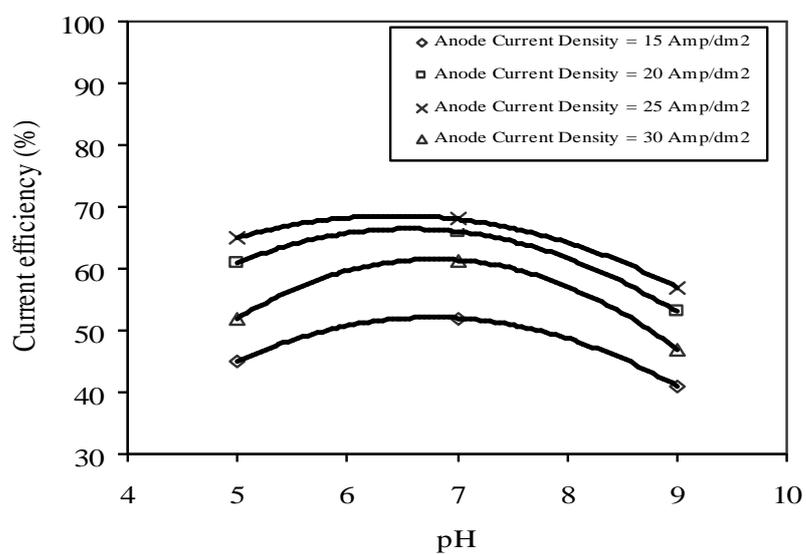
**Fig. (5):** Variation of Current Efficiency with Temperature as a function of Anode Current Density at pH=5



**Fig. (6):** Variation of Current Efficiency with Temperature as a function of Anode

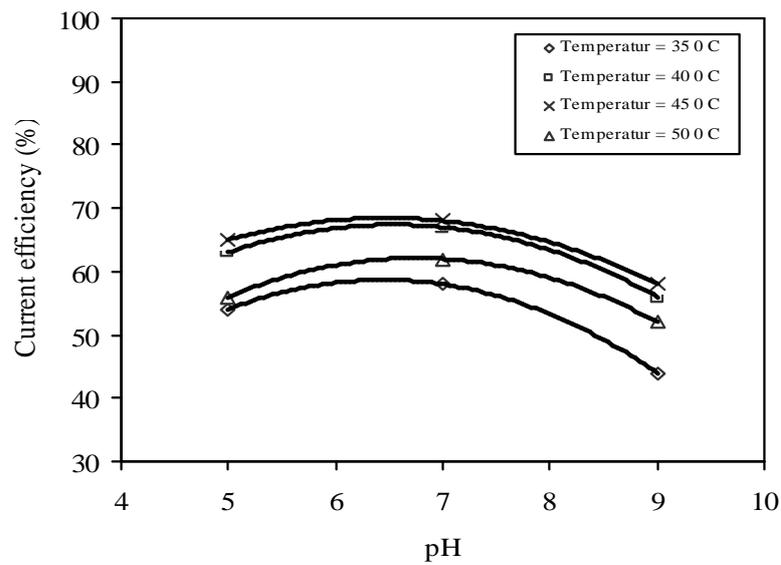


**Fig. (7):** Variation of Current Efficiency with Temperature as a function of Anode Current Density at pH=9



**Fig.(8):** Variation of Current Efficiency with pH as a function

**Fig. (8):** Variation of Current Efficiency with pH as a function  
Anode of Current Density at Temperature = 45<sup>0</sup>C



**Fig. (9):** Variation of Current Efficiency with pH as a function of Temperature at  
Anode Current Density = 25 Amp/dm<sup>2</sup>

## تصنيع البركلورات بالطريقة المباشرة باستخدام الكرافيت المغطى بثنائي أكسيد الرصاص

### (GSLD) كأنود

احمد دحام وهيب

مدرس

كلية الهندسة - جامعة تكريت

### الخلاصة

حضرت بيركلورات الصوديوم كهروكيمياوياً من كلوريد الصوديوم بخطوة واحدة بأمرار تيار مباشر خلال المحلول ، بتوفر العوامل المضافة ( مثل فلوريد الصوديوم ). وقد تم تصميم خلية الكتروليتية مختبرية للحصول على النتائج المختبرية لتحضير بيركلورات الصوديوم. محلول مكون من ( ٢٩٠ غم / لتر) من كلوريد الصوديوم و ( ٢ غم / لتر) من فلوريد الصوديوم يتم تحليله بالطريقة الدفعية . أستخدم الحديد المقاوم للصدأ ككاثود والكرافيت المغطى بثنائي أكسيد الرصاص كأنود . وقد تم دراسة تأثير كثافة التيار على الأنود ودرجة الحرارة ودرجة الحموضة للمحلول الالكتروليتي على كفاءة التيار لتكوين بيركلورات الصوديوم . تم الحصول على كفاءة تيار بحدود ٦٨% باستخدام (GSLD) كأنود.