

STUDY OF THE FACTORS AFFECTING CELLS OF SODIUM PERCHLORATE PRODUCTION

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ABSTRACT

The aim of this research work was to understand the basis of an existing perchlorate cells provided with platinum anodes belonging to an existing installation for the production of sodium perchlorate, and also to find the optimum operating conditions for perchlorate cell provided with graphite substrate lead dioxide (GSLD) anodes which are considered as the best alternative anodes to platinum.

A laboratory cell was designed and utilized to obtain experimental results which were necessary for the fulfillment of the designated objective of this work. A saturated solution of sodium chlorate is electrolyzed batch wise at a temperature ranging from 20 to 50 °C, an anodic current density ranging from 30 to 50 Amp/dm², and a current concentration ranging from 45 to 55 Amp/lit. Also the effect of addition agents was tested. A current efficiency of about 70-80% was obtained in alkaline conditions which are satisfactory in comparison with the costlier platinum-anode cell.

INTRODUCTION

Sodium perchlorate is the most important raw material of the preparation of perchlorate salts and perchloric acid. It can be produced both chemically and electrochemically. Commercially, sodium perchlorate is produced in an electrolytic cell^[1]. Ammonium perchlorate is used as an oxidizer in the propellant of rockets and missiles and is used in explosive and pyrotechnic formulation^[2,3]. Sodium perchlorate is used also in slurry blasting formulations^[4].

Electrochemical Process

Sodium perchlorate production system consists of electrochemical cells in which a concentrated solution (400 - 700 g/l) of sodium chlorate is subjected to electrolysis until the concentration of chlorate reaches a level below 5 g/l.

The anodic potential required for the formation of the perchlorate ion is high and secure this high potential early investigators used cells with smooth platinum electrodes. In general, the cell used for the commercial production of sodium perchlorate consists of a steel tank containing cooling coils and equipped with platinum anodes^[5].

The sodium chlorate solution flowing or is pumped from a storage tank to the cells in

parallel. The solution flows through the cell, is collected and returned to the storage tank, and when the sodium perchlorate concentration reaches the desired value, the product is collected and stored.

Most commercial cells are equipped with platinum anodes which are the most favored anodes because of their high oxygen overvoltage and low erosion and dissolution rates^[6,7].

Conventional Platinum Anodes Cell Specifications

Usually the conventional electrolysis cell using platinum anodes are specified by the following parameters^[5]:

- Temperature	35-45 °C.
- Feed rate	At least 10 l/min.
- pH	6-7.
- Feed to cell:	
Sodium chlorate	400 g/l.
Sodium perchlorate	400 g/l.
Sodium dichromate	5 g/l.
- Anode current density	31 Amp/dm ² .
- Cell voltage	6.5-7.0 V.
- Calcium and magnesium	As low as possible.
Final sodium chlorate concentration	As high as impurity removal in recovery will permit.
- Current efficiency	90-95%

The voltage drop across the perchlorate cell depends on: (1) anode material; (2) cathode-anode spacing; (3) concentration of reagents in the cell; (4) cell temperature; (5) current density on the anode and the cathode; and (6) cathode material. Because of the high anodic potential essential for the formation of perchlorate, the voltage drop across the cell is relatively high.

Applications of Graphite Substrate Lead Dioxide (GSLD) Anode

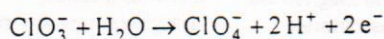
The high capital investment required by using the cells provided with platinum anodes leads to the necessity of searching for anode material suitable as a substitute for such costlier anodes.

The recent researches aimed for development of anodes either as a substitute for platinum anodes or to increase the life of anodes in electrochemical processes.

Lead dioxide satisfies the major requirements for the oxide anode. It has a high anodic potential for oxygen evolution and it is inert for most chemical solutions. Therefore, the anode formed by electrodeposition of lead dioxide on graphite substrate (GSLD) from an aqueous lead salt bath is the only alternative anode to platinum for the production of perchlorate. The lead nitrate bath is preferred, since it gives a high-quality deposit over a relatively wide range of operating conditions^[7]. Recent work has been concentrated on improvement in the process for electrodepositing lead dioxide for increasing the current efficiency of the electrochemical process using it.

Preparation of Sodium Perchlorate by Electrochemical Process

Sodium perchlorate is prepared electrochemically by using an electrolytic cell, which consists of anode and cathode electrodes. The electrolytic cell reaction can be written as follows:



Some oxygen is produced at the anode and is the main reason of the inefficiency of the process. Hydrogen is produced also from reduction of water at the cathode^[4].

As for other oxidation reactions, there are two possible pathways along which chlorate conversion may proceed, one of these called the primary reaction mechanisms, which involves a direct electron withdrawal from the chlorate ion, as a first step, followed by a homogeneous reaction of the free radical with water. The second possible pathway called the secondary reaction mechanism, the water molecule would be involved in the charge transfer step, with the production of surface oxides (or adsorbed oxygen-containing species, e.g., OH or O). Such materials would then perform as oxidants of the chlorate ion diffusing towards the substrate or being coadsorbed at the electrode surface^[8].

Sugino and Aoyagi^[9] were the first to investigate the correlation between anode potential and current density. By their method, which was essentially potentiokinetic, they were able to observe two stages of potential in 1.4M NaClO₃ at 17 °C by using platinum microanode. Since the first stage, occurring between 1.7 and 1.9 V corresponds (mostly) to oxygen evolution and the second stage, higher than 2.3 V, corresponds (mostly) to chlorate oxidation. The authors interpreted their results by assuming that chlorate oxidation proceeds through a primary discharge step.

Narasimham, Sundarajan and Udupa^[10] investigated the influence of addition agent and duration of electrolysis on current efficiency of perchlorate formation by using GSLD as anode and stainless steel as cathode. They observed that the current efficiency was improved so much with using 2 grams per liter of NaF in the electrolyte. Osuga et al.^[11] studied the relation between anode potential and current efficiency using platinum and pure lead dioxide anodes. They observed that the current efficiency on platinum anode was higher than that on the pure lead dioxide anode (95%, 85% respectively), due to the higher anode potential of platinum.

EXPERIMENTAL WORK

The experimental work for this study can be divided into two parts; the first part deals with the preparation of GSLD anode and the second with the preparation of sodium perchlorate using the prepared GSLD anode.

Electrochemical System for the Preparation of GSLD Anode

Electrochemical system used for the preparation of cylindrical GSLD anode is explained elsewhere^[12] and shown in Fig. 1. It consists of electrolytic cell which in turn consists of cell body, anode, cathode, agitator, D. C. power supply, multi-range voltmeter, thermometer, and tachometer. The anode assembly used in the experiments is shown in Fig. 2.

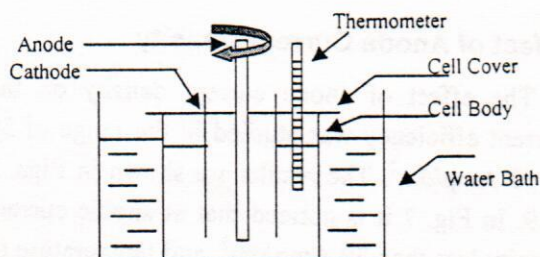


Fig. (1) The electrochemical system for the preparation of GSLD anode

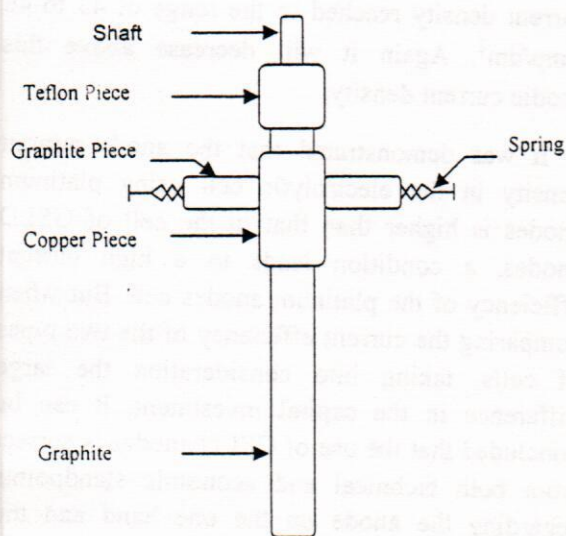


Fig. (2) Anode used in the preparation of GSLD electrode

Electrochemical System for the Preparation of Sodium Perchlorate

The electrochemical system used for the preparation of sodium perchlorate is explained elsewhere^[16] and shown in Fig. 3. It consists of electrolytic cell, containing GSLD anode and perforated stainless steel cathode, reference electrode, thermocouple, chiller for electrolyte cooling, on-off controller, and a cell cooler.

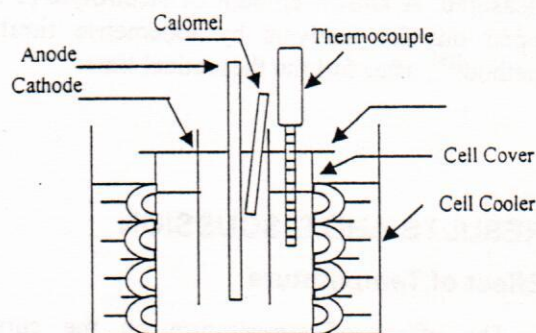


Fig. (3) The electrochemical system for the preparation of sodium perchlorate

Experimental Technique

It is most important to have pre-cleaning operation for graphite anode prior to electrodeposition. The pre-cleaning process was done by electrolyzing a 10% (W/V) sodium hydroxide solution with the graphite as anode and copper as cathode for 30 min, followed by dipping the anode in 10% (V/V) nitric acid for 10 min, and finally washing it thoroughly with distilled water^[12].

The cathode was pre-cleaned to remove oxide from its surface. The pre-cleaning was done by dipping the cathode in 10% (w/v) sodium dichromate and 5% (W/V) sulfuric acid for 10 min, and finally washing it thoroughly with distilled water^[13].

The electrolyte composition used in this work is^[14]: Lead nitrate $Pb(NO_3)_2$; 350 g/l, and copper nitrate $Cu(NO_3)_2 \cdot 3H_2O$; 30 g/l.

Electrolyte was prepared according to the following procedure: the required weights of components are put in the volumetric flask of 1 liter and then half amount of warm distilled water,

then stirring until dissolved completely, then the remaining quantity of distilled water was added with stirring the electrolyte. The bath pH is about 4 to 4.5.

The electrolytic cell was first filled with 200 ml of electrolyte in each experiment, then the anode and cathode 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 on-off controller was operated to adjust the temperature of the electrolyte. At the end of the theoretical time of electrolysis, the pH of electrolyte was measured. A known amount of electrolyte (5 ml) piped out for analysis by iodometric titration method^[15], after full the theoretical time.

RESULTS AND DISCUSSION

Effect of Temperature

The effect of temperature on the current efficiency was studied in the range of 20 to 50 °C. The results are shown in Figs. 4 to 6 and similar effects were shown for these figures. In Fig.4 it is observed that at temperature lower than 20 °C at an anodic current density of 40 Amp/dm², the current efficiency decreases to less than (69%), while at temperature higher than 20 °C the current efficiency increases until it reaches a maximum at 36 to 40 °C. After this the current efficiency decreases again. This can be interpreted as follows: the rate of decomposition of chloric acid (HClO₃) depends on the anode layer pH. According to Oechsli^[16], stability of chloric acid is favored greatly by diminished acidity. Therefore, it is necessary to consider the effect of rise in temperature on anode layer pH. Due to electrode reaction, anode layer pH would be lower than bulk pH. The extent of lowering, however, would depend on diffusion which in turn is dependent on temperature.

Higher temperatures would be expected to cause a rise in anode pH due to increased rate of diffusion and increasing of current efficiency. It is well known that all chemical reactions are accelerated by a rise in temperature due to activation energy effect. This is also true for the decomposition of chloric acid. Therefore, it is to be expected that a rise in temperature should cause an increased rate of decomposition and lowering of current efficiency^[10]. From the above

discussion, it is clear that the rise in temperature has two opposite effects on current efficiency, therefore, the increase in temperature increases the diffusion process which leads to an increase in anode layer pH which cause an increase in the chloric acid stability and the current efficiency will increase. On the other hand, the increase in temperature increases the rate of decomposition of chloric acid due to the activation energy effects, and this will decrease the current efficiency, therefore, the net effect would depend on which of the two would predominate. The rise of current efficiency with temperature up to the optimum may be due to the first factor predominating over the second, whereas above the optimum temperature the opposite trend is to be interpreted as due to the predominance of the second factor.

The above results are in agreement with Narasimham^[10] who showed that the current efficiency is affected differently depending on whether acidic or alkaline pH conditions are used to start with.

Effect of Anode Current Density

The effect of anode current density on the current efficiency was studied in the range of 30 to 50 Amp/dm². The results are shown in Figs. 7 to 9. In Fig. 7 it is noticed that at anodic current density less than 30 Amp/dm², and temperature of 40 °C the current efficiency reduces to less than 77%. On the other hand, at the anodic current density higher than 30 Amp/dm² the current efficiency increases to the extent that the anodic current density reached to the range of 43 to 46 Amp/dm². Again it will decrease above this anodic current density.

It was demonstrated that the anode current density in the electrolytic cell using platinum anodes is higher than that in the cell of GSLD anodes, a condition leads to a high current efficiency of the platinum anodes cell. But when comparing the current efficiency of the two types of cells, taking into consideration the large difference in the capital investment, it can be concluded that the use of GSLD anodes is correct from both technical and economic standpoints regarding the anode on the one hand and the whole process on the other hand.

Effect of Current Concentration

The effect of current concentration on current efficiency was studied in the range of 45 to 55 Amp/l. The results were explained in Figs. 10 to 13.

It can be seen that the relation between current concentration and current efficiency of different values of temperature and anodic current density have the same behavior. In Fig. 10 it is observed that at current concentration 45 Amp/l the current efficiency is high and slightly decreases with increase of current concentration. Also it can be seen in Table 2 that bath voltage increasing with increasing current concentration. Therefore, the optimum current concentration which gives a high current efficiency is 45 Amp/l.

The results can be interpreted as that increasing current concentration causes an increase in the rate of decomposition of chloric acid therefore, reducing the current efficiency.

Effect of Addition Agents

The addition agents, in general, are used in the perchlorate cells to increase the oxygen overvoltage of the anode and also to increase the current efficiency of the process. The selection of the agent, which is added, highly influences the

efficiency of the production process. Some agents were employed to achieve the above purpose. In acidic condition of electrolysis, HCl or H₂SO₄ may be used as addition agents. The effect of addition of H₂SO₄ (3.11N) and HCl (3.11N) for acidic conditions on conversion of chlorate to perchlorate is shown in Table 1. It is obvious that using H₂SO₄ to control the pH of the solution gives better current efficiency than that when using HCl. This may be due to the oxidation of SO₄²⁻ ions to S₂O₈²⁻ ions which in turn gives better current efficiency as concluded by Bennet and Mack^[17].

The presence of 2 g/l of NaF markedly raises the current efficiency in alkaline conditions as shown in Table 1, because it inhibits the O₂ evolution and also improves ClO₃⁻ conversion. The above results, with particular regard to Table 1 show that the current efficiency is strongly influenced by the presence of addition agents.

Optimum Conditions

From the above results, the optimum conditions of electrolysis of sodium chlorate to produce sodium perchlorate in an electrolytic cell provided with a GSLD anode can be given in Table 2.

Table (1) Effect of addition agents on current efficiency. anode, GSLD; cathode, stainless steel; vol. of electrolyte, 200 ml; anode current density, 23.2 amp/dm²; current concentration, 35 amp/lit; temperature, 30 °C.

Exp. No.	Initial chlorate conc., g/l	Final chlorate conc. after theor. time, g/l	Addition Agent	Current efficiency %
1	603.2	314.0	10 ml of 3.11N HCl	47.0
2	603.2	235.9	3.5 ml of 3.11N H ₂ SO ₄	60.9
3	603.2	180.9	2 g/L of NaF + 6.1 ml of 3.11N of HCl	70.0
4	603.2	150.8	2 g/L of NaF + 2.8 ml of 3.11N of H ₂ SO ₄	75.0
5	603.2	211.1	No addition agent	65.0
6	603.2	141.9	2 g/lit of NaF	76.5

Table 2 The optimum conditions for the preparation of sodium perchlorate

Characteristics	Value
Anode current density, (Amp/dm ²)	43-46
Electrolyte temperature, (°C)	35-40
Current concentration, (Amp/lit)	45
pH	8-11
Addition agent, NaF, (g/L)	2
Anode material	GSLD
Cathode material	Stainless steel
Space between anode and cathode, (cm)	1.5
Bath voltage, V	4.5-5.5

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CONCLUSIONS

The factors affecting the chlorate oxidation process to produce perchlorate in a cell provided with graphite substrate lead dioxide (GSLD) anode, subject of this research work, were determined. Conclusions drawn from this work are:

1. Electrodeposited lead dioxide on graphite substrate led to producing an inert and insoluble anode, which gave high current efficiency of the perchlorate process. It can be concluded that this anode is an efficient alternative of conventional platinum anode.
2. High current efficiency (about 80%) was obtained in alkaline conditions.
3. Using of addition agent (2 g/l NaF) enhance the current efficiency in the alkaline conditions.
4. Study of the effect of temperature led to the result that the highest current efficiency is attained at a temperature range of 36-40 °C. A remarkable difference was found between platinum and lead dioxide. In the case of platinum it has been reported that higher temperature ranges are utilized which gives higher current efficiency.
5. The anode current density is an efficient parameter of the perchlorate cell process. Its optimum value was found to be between 43 to 46 Amp/dm², while the current concentration showed a small effect on the process current efficiency.

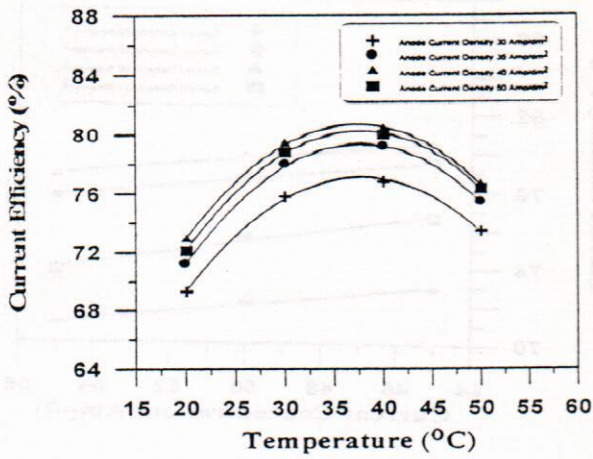


Fig. (4) Influence of temperature on current efficiency at current concentration 45 Amp/lit

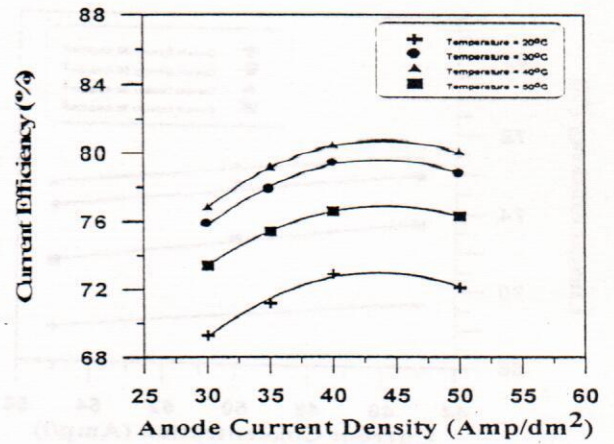


Fig. (7), Influence of anode current density on current efficiency at current concentration 45 Amp/lit

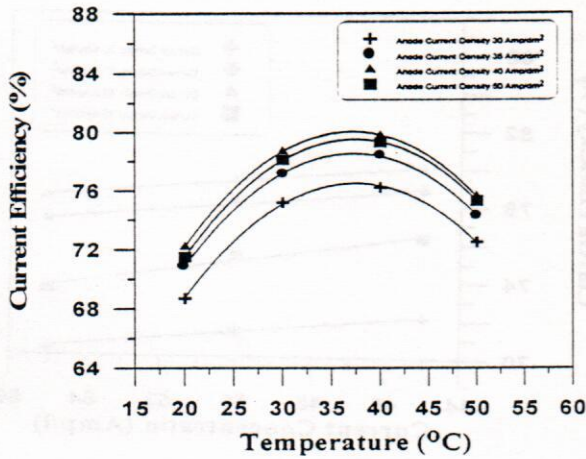


Fig. (5), Influence of temperature on current efficiency at current concentration 50 Amp/lit

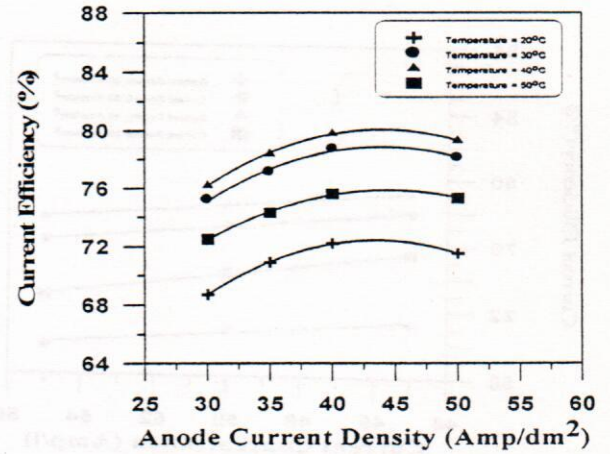


Fig. (8), Influence of anode current density on current efficiency at current concentration 50 Amp/lit

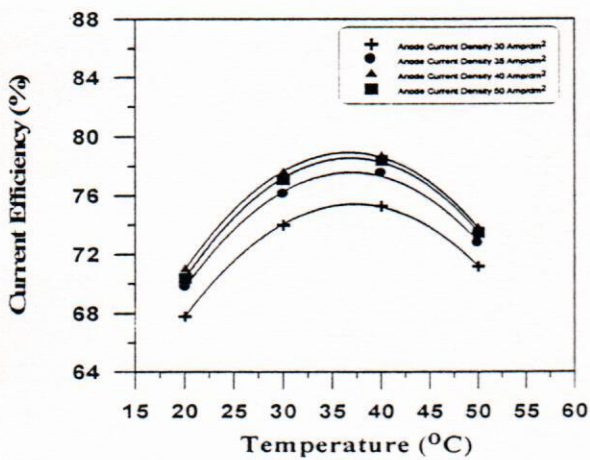


Fig. (6), Influence of temperature on current efficiency at current concentration 55 Amp/lit

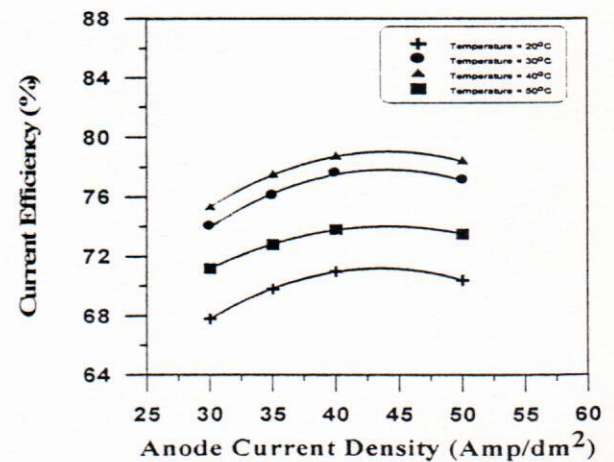


Fig. (9), Influence of anode current density on current efficiency at current concentration 55 Amp/lit

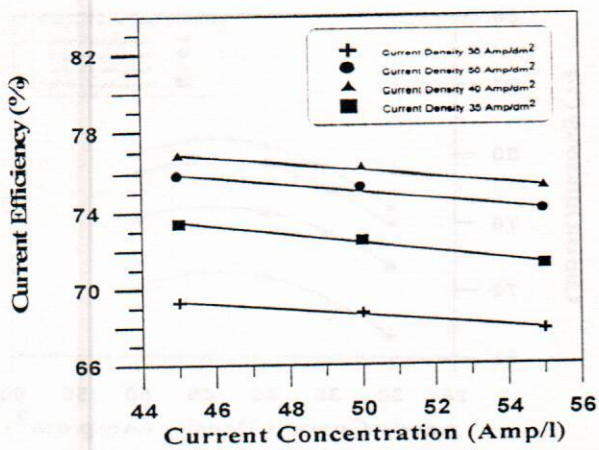


Fig. (10), Influence of current concentration on current efficiency at temperature of 20°C

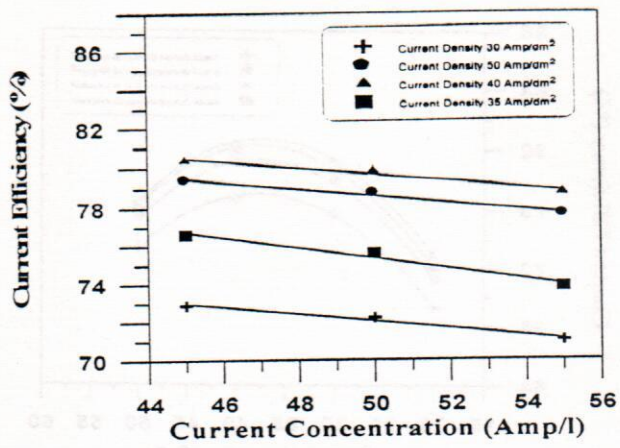


Fig. (12), Influence of current concentration on current efficiency at temperature of 40°C

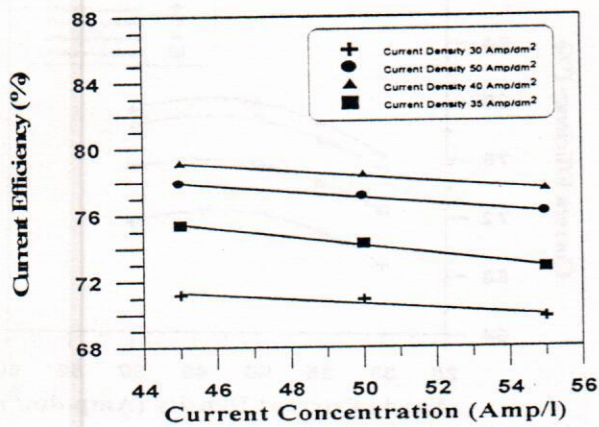


Fig. (11), Influence of current concentration on current efficiency at temperature of 30°C

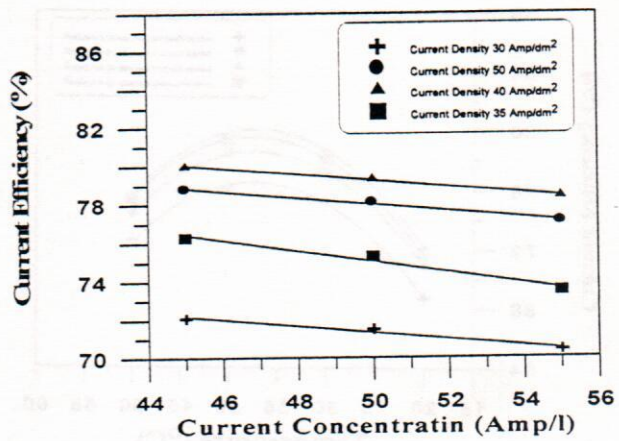


Fig. (13), Influence of current concentration on current efficiency at temperature of 50°C