STUDY OF THE FACTORS AFFECTING CELLS OF SODIUM CHLORATE PRODUCTION

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ABSTRACT

The present research aims to express the basis working fundamentals of an existing chlorate cells providing with titanium electrodes belonging to an existing installation for producing sodium chlorate. It aims also to study the main factors affecting the efficiency of the chlorate cell process.

The experimental design of Box-Wilson method was adopted to find a useful relationship between the current efficiency as a system response and the three controllable variables, namely; system temperature, solution acidity and electrolyte flow rate. The experimental data obtained is successively fitted to a second order polynomial mathematical model. Furthermore, selective extra experiments were carried out to investigate the effect of anodic current density on the process current efficiency.

A laboratory cell system with metal-coated titanium anode was designed and utilized to obtain experimental results necessary for the fulfillment of the designated objective of this work.

In the present experiments, 290-300 g/l of sodium chloride solution was electrolyzed in a close loop system at temperatures ranged from 30 to 80°C, anodic current density ranged from 0.04 to 0.4 A/cm2, solution acidity ranged from 5 and 8 and electrolyte flow rate ranged from 8 to 38 l/hr. A current efficiency of about 99-91% was obtained at system temperature of 75-80°C, solution acidity of 6.1-6.3, electrolyte flow rate of 21-28 l/hr and anodic current density of 0.22 A/cm^2.

INTRODUCTION

Production of chlorate has increased enormously during the past twenty-five years and appears to continue to increase at an accelerated rate in the years ahead. This growing has brought increased competition among producers and thus has created new demands for better technology and higher standards of production efficiency.

In general, and from chemical point of view, chlorate are salts of chloric acid (HClO3), and sodium chlorate (NaClO3) forms white cubic crystals which have a melting point of 248 oC, decomposition point of 265 oC and specific gravity of 2.48.

On thermal decomposition, sodium chlorate may produce the corresponding perchlorate, and the molten salts are powerful oxidizing agents. On the other hand, the mixture of chlorate with organic materials have been employed as explosives, however, a mixture of sodium and potassium chlorate with any combustible organic or inorganic materials should be regarded as dangerous.

The electrochemical production of sodium chlorate is characterized by the anodic oxidation of chloride ions in the starting raw material (usually sodium chloride) in electrochemical cell without diaphragms where the chlorine produced at the anode, is hydrolyzed to hypochlorite. The hypochlorite reacts with hypochlorous acid to produce the final product, chlorate. Hydrogen is the cathode product at this electrochemical process

Anode oxidation of hypochlorite, as one of the many parallel and competing possible paths in the electrolytic production of chlorate, is accompanied by oxygen evolution, and the corresponding current losses directly proportional to the hypochlorite ion concentration. In fact, there are more than twelve side reactions with different mechanisms may taking place between the chemical species present in the electrochemical chlorate cell themselves as well as between these species and the electrodes. These side reactions may cause current losses and seriously reduce the current efficiency of the cell.

The main factors that affect both main and side reactions are the current density, system temperature, electrolyte solution acidity, hypochlorite concentration and the hydrodynamic condition of the system. Therefore, one has to seek intermediate optimal conditions to yield the maximal current efficiency for chlorate production. However, the major portion of the oxidation and reduction reaction losses in the chlorate cell, comes from the hypochlorite species[3].

At the present time, the electrolytic cells of sodium chlorate production are undergoing rapid changes as a result of the development of noble metal-coated titanium anode which uses RuO_2, TiO_2, IrO_2 or PtO_2 electrocatalyst coatings on titanium substrates. Besides the quite advanced polarization properties of the metal-coated titanium anode in chlorate cell process, a high current density – up to 0.3 Amp/cm^2 can be used, also, a higher system temperature level can be adopted, with a negligible corrosion effect on the anode characteristics at high temperatures [1,4].

A chlorate cell system requires five simple units, process zones as illustrated in Fig.1 and described below [].

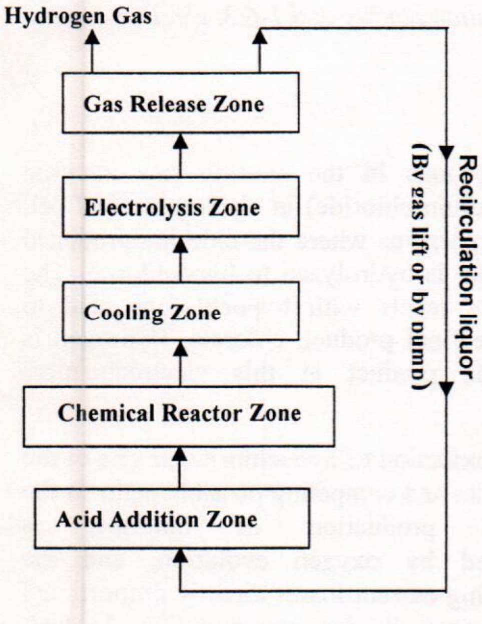

Figure. 1 Units of Chlorate System Reactions

EXPERIMENTAL WORK

A schematic diagram of the experimental equipment used in this work is shown in Fig 2 and the general arrangement of the electrolytic cell is shown in Fig.3. The electrochemical system consists of the following laboratory equipment

The electrolyzer consists of the following parts as shown in Fig. 2 The cell body was made of perspex glass plates of thickness (1, 0.5 and 0.1 cm). The plates arranged to form a rectangular shape box having internal dimensions of 12 cm height, 16.5 cm length and 3.5 cm width. The Perspex plates were bonded together by two screws in each corner and the space between the corners was filled with epoxy.

The rectangular cell body have two circular holes from its opposite side with 1.5 cm internal diameter, two tubes made of Pyrex glass were inserted in the holes, to allow the solution passing through in and out the cell body. The inlet tube was at height 4 cm and the outlet tube was of height 9.5 cm from the bottom of the cell body.

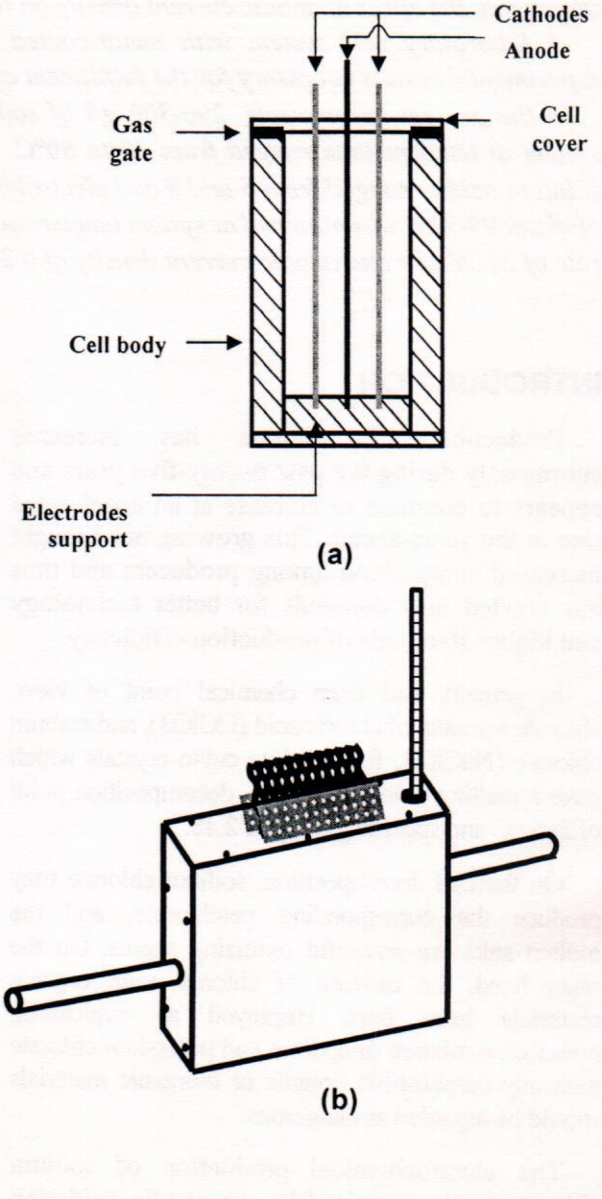

Fig. 2 The Electrolyzer

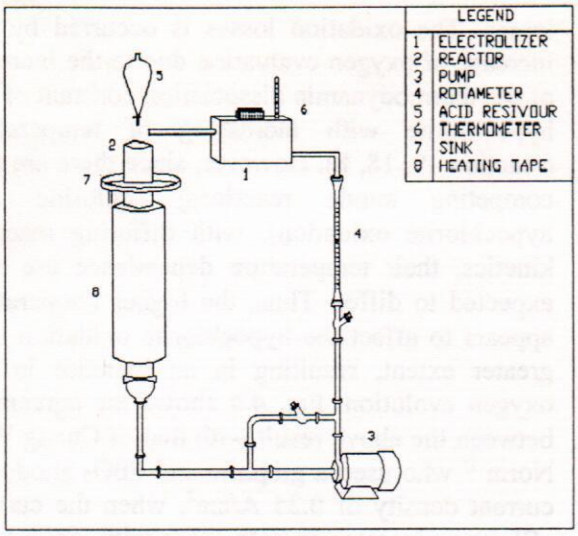

Fig. 3 Experimental Equipment

Experimental Procedure for Preparation of Sodium Chlorate

The effect of operating temperature, flow rate and solution acidity on the current efficiency were investigated and analyzed using the experimental design. Box-Wilson central composite design was used to find a suitable relationship between the three independent variables and the observed response.

In addition to the experimental design experiments (Box-Wilson) many other experiments were carried out at selected conditions. In order to reify the results obtained. The conditions of these experiments were shown in Table 1.

Table1. Conditions of extra Experiments

Exp.No.	Experimental variables	Variable range	Experiment's conditions
16	Current density	0.04-0.4 A/cm^2	pH = 6.1-6.3, flow rate = 24 l/hr, temp. = 78-80 °C
17	System temperature	30-80 °C	pH = 6.1-6.3, flow rate = 24 l/hr, C.D = 0.22 A/cm^2
18	pH	5.4-6.9	Temp. = 78-80 °C, flow rate = 24 l/hr, C.D = 0.2 A/cm^2
19	Flow rate	11-36 l/hr	Temp. = 78-80 °C, pH = 6.5-6.7, C.D = 0.22 A/cm^2

Description of the Preparation Procedure

At the beginning, the electrodes were pre-cleaned using 0.1 N HCl solution and they were dried by air, then, the NaCl solution which was heated early, was placed into the system. The pump was operated to obtain the desired flow rate. The heating tape was operated to rise the solution temperature to the desired value. Then, power supply was switched-on to provide a constant current.

0.5-0.7 N HCl, was added to the solution continuously to maintain the acidity of the solution within the desired range.

The electrolyte volume was measured and Iode metric titration method was used for the analysis of the electrolyte solution after the theoretical time of cell operation.

The study of sodium chlorate process was carried out in a laboratory cell furnished with DSA anode. as far as this study is concerned, analysis of the chemical and electrochemical reaction that occurred in the cell was mainly concentrated on the current efficiency. However, the effects of temperature, solution acidity, current density and electrolyte flow rate on the current efficiency were studied as the main variable affected the chlorate cell process according to the data available in literature.

RESULTS AND DISCUTION

A set of experiments were conducted to find the effect of temperature flow rate, electrolyte solution acidity and anodic current density on the current efficiency of the chlorate cell process.

Postulating the Mathematical Model

The response of experiments conducted according to Box-Wilson method, which represented by current efficiency, are fitted to a second order polynomial mathematical model. This model is employed in the range of the three independent variables (system temperature, electrolyte solution acidity and flow rate)

To postulate the best formal of the proposed models, the experimental data were fitted and nonlinear regression analysis was adopted to estimate the coefficients of the proposed model. Using the experimental data the coefficients of the 2nd order polynomial were estimated by implementing nonlinear regression analysis technique via statistical software. The number of iteration were terminated when the proportion of variance accounted for was equal to 0.915 and the correlation coefficient R was equal to 0.9568, correlating the three variables with current efficiency, the following models were determined.

$$y = -1.12346 + 0.009542x_1 + 0.484987x_2 + 0.012834x_3 - 0.000068x_1^2 - 0.037899x_2^2 - 0.000274x_3^2$$

where:

x_1 is the system temperature
x_2 is the solution acidity
x_3 is the flow rate

Current Efficiency in the Formation of Sodium Chlorate

The investigation was carried out with particular regard to intermediate conditions that are met with industrial $NaClO_3$ production. Accordingly, the temperature was taken in the range of 3 to 80 °C, solution acidity (pH) 5 to 8, current density of 0.04 to 0.4 A/cm^2 and flow rate of 8 to 38 l/hr. The concentration of NaCl solution was maintained at about 290-300 g/l through the experiments. The effect of each variable on the current efficiency is discussed in the following subsections.

Effect of System Temperature

The effect of system temperature was experimentally studied in the range of 30 to 80 °C. Fig. 4 shows this effect on the current efficiency at constant pH, anodic current density and flow rate. Fig. 5 shows the effect of temperature on the current efficiency at different pH values, and Fig. 6 shows the effect of the system temperature on the current efficiency at different electrolyte solution flow rates

From Fig. 4, it can be seen clearly that the current efficiency decreases to lower than 82% when the system temperature is decreasing below 30 °C, at pH of 6.1-6.3 and current density of 0.22 A/cm2 and then it increases as the system temperature is increasing. The increase of current efficiency is due to the increase of the rate of chemical conversion of the hypochlorite and hypochlorous acid to chlorate , which represents a slow reaction in which the reaction rate constant increase markedly with increasing of system temperature. Another asymptotic level, the effect of the temperature on the current efficiency is very clear at temperatures above 65 °C. This is much more pronounced when it compared with the increasing of the current efficiency at temperatures below 60 °C. These results can be explained by the fact that the increase in temperature leads to increase of the oxidation losses. The oxidation losses is occurred by the increase of oxygen evaluation due to the increase of the thermodynamic dissociation constant of the hypochlorite with increasing of temperature (reaction 19, 18, 8). However, since there are two competing anode reactions, (chloride and hypochlorite oxidation), with differing reaction kinetics, their temperature dependence are also expected to differ. Thus, the higher temperature appears to affect the hypochlorite oxidation to a greater extent, resulting in an increase in the oxygen evolution. Fig. 4.4 shows the agreement between the above result with that of Chang Woa Norm [0] who used a graphite and PbO_2 anodes at current density of 0.25 A/cm^2, when the current efficiency increase in both cases with increase of system temperature, no matter what the metal what the metal of anode material.

Effect of the Acidity of Electrolyte Solution

The effect of the solution acidity in the range of 5 to 8 was studied. Fig.8 shows this effect on the current efficiency for different flow rates. Fig.9 shows the effect of the solution acidity on the current efficiency at different system temperatures, while Fig.10 shows the above effect in the range of 5.3 to 6.8 on the current efficiency at constant system temperature, current density and electrolyte flow rate.

From Fig. 10, it can be observed that the pH lower than 5.3 and temperature of 78-80 oC, the current efficiency decreases to less than 86%, while at pH higher than 5.6 the current efficiency increases until it reaches a maximum of 91% of pH of 6.1-6.3. After this the current efficiency decreases again.

This effect can be interpreted as follows: in acid solution the hypochlorous species decomposes and its concentration decreases until reaching negligible concentration (in very acid solution). Then chlorine evolution approaches its maximal current yield (reaction 28).

$$HOCl + HCl \rightleftharpoons H_2O + Cl_2$$

In this case, the chlorate efficiency has a small value, and the whole cell operates as a chlorine producing unit.

On the other hand, in very alkaline solution, the hypochlorous acid concentration approaches zero, and all active chlorine build up its concentration and exists is the form of hypochlorite ions. This reduces the chemical conversion of available to a negligible rate, so that, the final effect represents chlorate production taking place from total anodic oxidation only. Hence, the current efficiency will decreases in any case that approach to the two limiting cases above (very acid solution and very alkaline solution).

In the limiting cases discussed above, neither the temperature and the current density, nor any other operating variable and parameter could bring about a significant improvement of the chlorate cell efficiency, as shown in Figs. 8 and 9.

Effect of Current Density

The effect of the anodic current density on the current efficiency was studied in the range of 0.04 to 0.4 A/cm^2, the results are show in the Fig11, it is noticed that at anodic current density less than 0.043 A/cm2 temperature of 78-80 °C and pH of 6.1-6.3, the current efficiency reduces to less than 87.5%. On the other hand, the current efficiency increases to about 90.6% at anodic current density of 0.1 A/cm2 and begins to attain stable value of 91% at the remainder range.

What more, shows the increasing in bath voltage with increasing anodic current density.

The results can be clarified as follows. At low anode current density (i.e. 0.04 A/cm2 or lower) the potential does not attain a high value enough for (Cl^-) ions oxidation to occur at an appreciable rate, where the current losses were caused by the oxidation of (ClO^-) ions at the anode surface, and resulting in decreasing of the current efficiency. In fact, if the other conditions being equal, the discharge of (ClO^-) ions require less positive potential than that of (Cl^-) ions, even if the overall tensions are take into consideration.

For this reason a high current density is preferred in order to increase the discharging of (Cl^-) ions, keeping in mind the oxidation losses of the current efficiency at high current density and low chlorine concentration.

The above result was compared with work of Jasksic () who obtained the current efficiency in a platinum anode cell. Fig. 12 shows that, the platinum anodes needs more positive tension to discharge (Cl^-) ions than that of DSA anode. The current efficiency in platinum anode cell becomes stable in a current density higher than that needed in DSA anode. The same advanced polarization characteristics of DSA anode will appear when it compared with graphite anode.

Effect of Electrolyte Flow Rat

The motion of the electrolyte in the chlorate cell process is one of the important factors affecting the current efficiency of the cell. The effect of electrolyte flow rate on the current efficiency was experimentally studied in a range of 8 to 30 l/hr.

Fig. 13 shows the effect of flow rate on the current efficiency at different system temperature and Fig. 14 shows the above effect on the current efficiency at constant system temperature and solution acidity.

It can be seen from Figs. 13, 14 that the current efficiency is decrease to lower than 86% when the flow rate reduces to lower than 11 l/hr a solution acidity of 6.5-6.7 and system temperature of 76-80 °C, and it begin to increase to 89.5% in flow rate of 15 l/hr, then the current efficiency have some maximum of 90% at flow rate of 25 l/hr. A further increase in solution flow rate (> 30 l/hr) make the current efficiency to decrease less than 87%.

This result can be interpreted as that, increasing of the flow rate will increase the current efficiency due to the reducing of the hypochlorite species that present in the cell which will decrease the anodic discharge of (ClO^-) ions. In fact, namely, due to the subsequent chlorine hydrolysis, which prevalently takes place within the diffusion layer, hypochlorous species diffuse in both directions from and toward the generating electrode. Thus, creating a certain concentration maximum inside the diffusion layer.

Hence, in order to really provide the concentration polarization, the diffusion layer should be cut down from the solution side by increasing the velocity of electrolyte that will lead to an increase in the hypochlorite species which enters the reactor and decrease in this species in the electrolyzer zone, which avoids a further anodic oxidation.

At higher solution flow rate (> 30 l/hr) it is seen that the current efficiency will reduce to a lower value, a condition that can be interpreted as that, the increase in the flow rate at same reactor volume will lead to a less residence time needed for the conversion of active chlorine to chlorate, and this increases the bulk concentration of active chlorine in the electrolyzer zone which causes further anodic oxidation and then to a low current efficiency of the process.

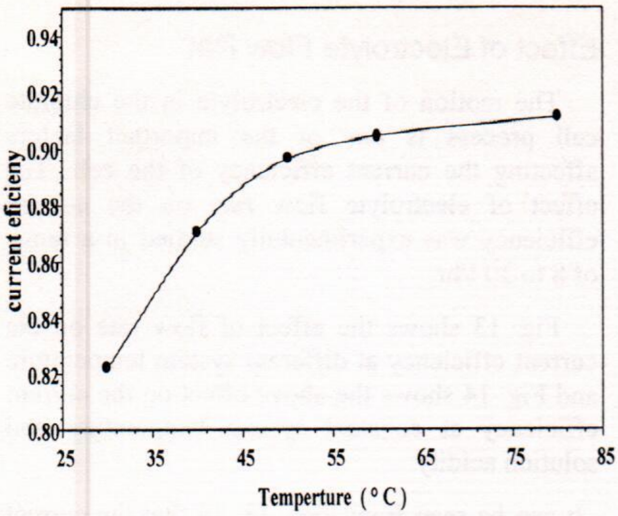

Fig. 4 Influence of system temperature on the current efficiency. C.D = 0.22 (A/cm^2) ;Q= 24 (l/h) and pH=(6.1-6.3)

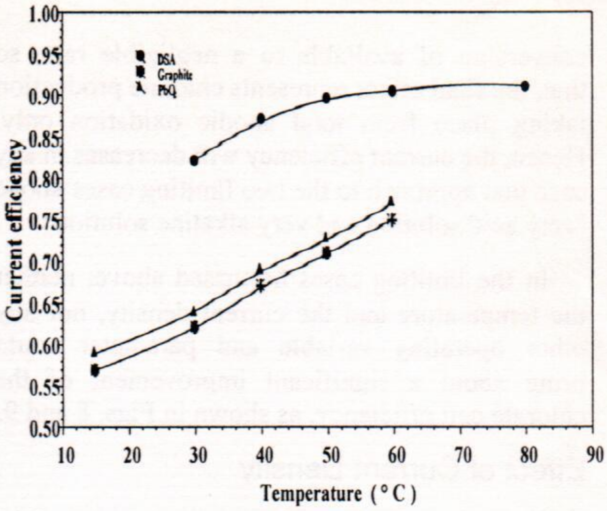

Fig.7 Effect of system temperature on the current efficiency with different anode Mattel

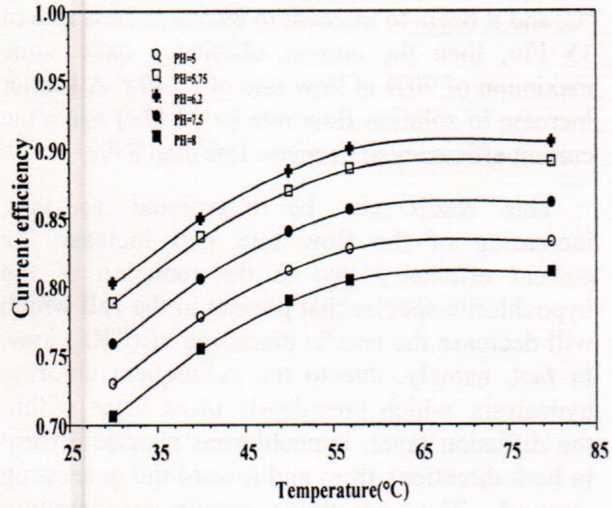

Fig 5 Influence of the system temperature on current efficiency at different solution acidity and electrolyte flow rate of 24 (l/h)

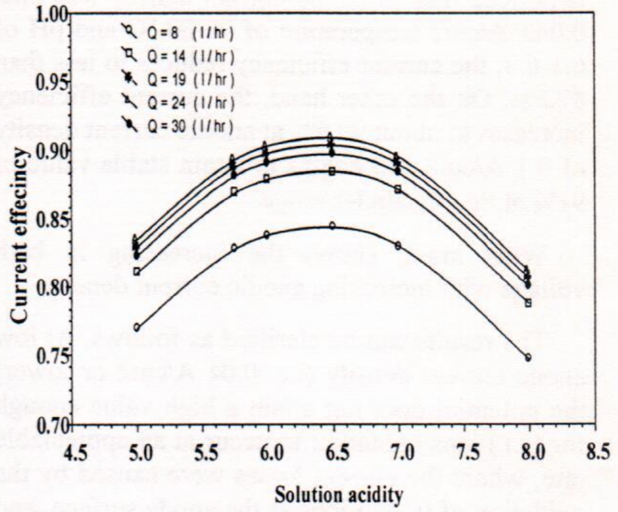

Fig 8. Influence of the solution acidity on current Efficiency at different electrolyte flow rate and system temperature of 78-80 °C

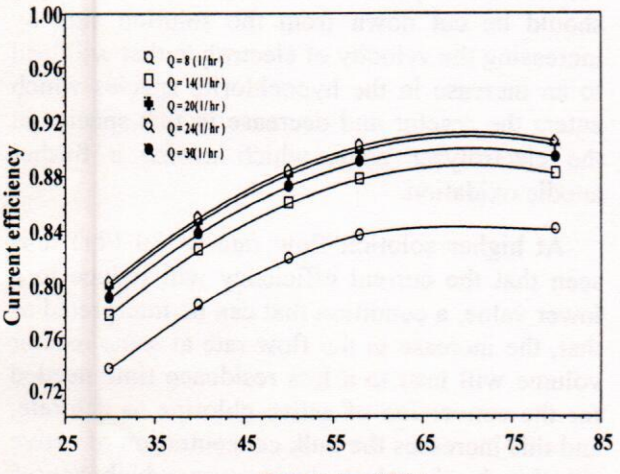

Fig 6 influence of the system temperature on current efficiency at difference electrolyte flow rate and solution acidity of 6.1-6.3

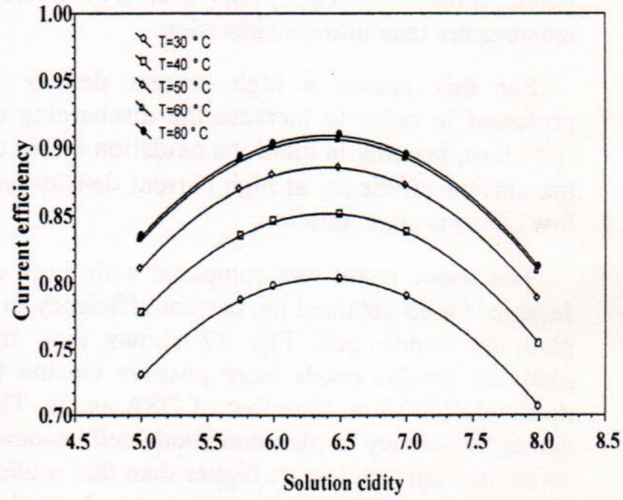

Fig 9. Influence of the solution acidity on current efficiency at different system temperatures and electrolyte flow rate of 24 (l/hr)

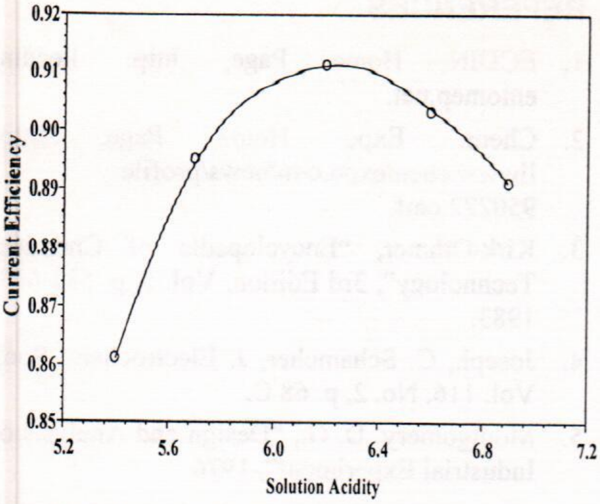

Fig .10 influence of solution acidity on current efficiency (T=78-80 °C ,Q=24 (l/h)and PH=6.1-6.3)

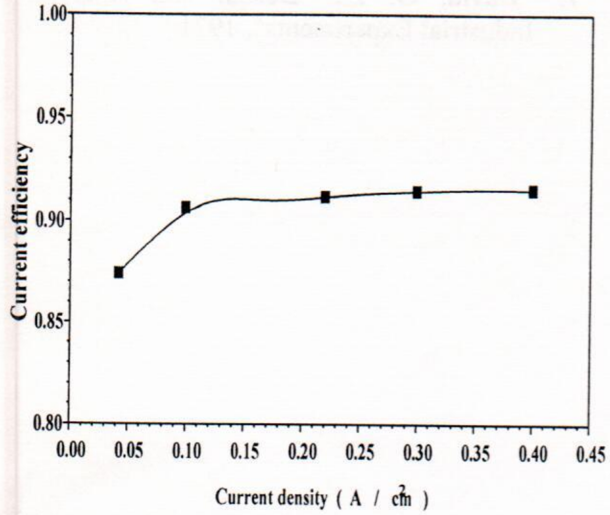

Fig11. Influence of anodic current density on current Efficiency (T=78-80 °C ,Q=24 (l/hr) and pH= 6.1-6.3)

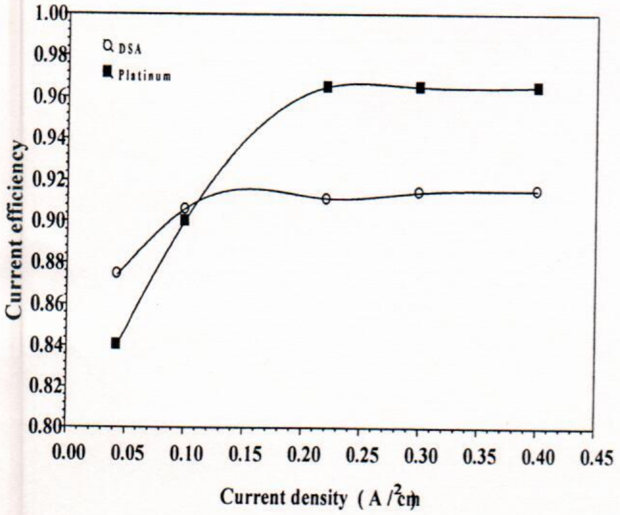

Fig 12. Influence of anodic current density on current Efficiency for DSA and Platinium Anodes

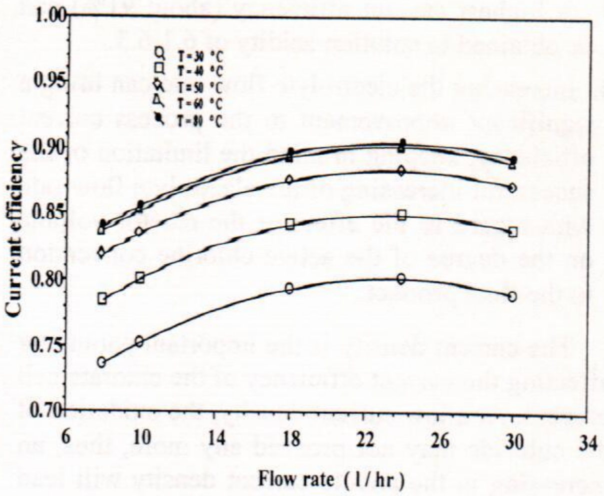

Fig 13 influence of flow rate on current efficiency at different system temperature and solution acidity at flow rate of 24 l/hr

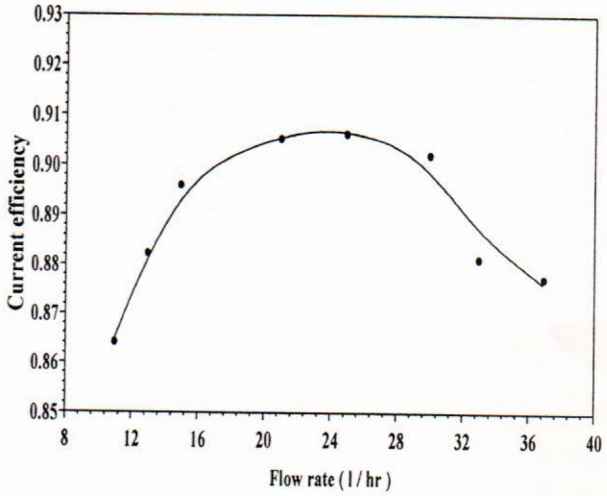

Fig (14) Influence of the flow rate on current efficiency at different system temperature and solution acidity of 6.1-6.3

CONCLUSIONS

The factors affecting the current efficiency in the production of sodium chlorate in a cell provided with metal-coated titanium anode, subject of this research work, were determined. Conclusions drawn from this work are:

1. Metal coated-titanium anodes are the favor metallic anodes in the chlorate industry, because of its advanced polarization characteristics to the oxidation of chloride ions to chlorine, compared with other electrodes.
2. Increasing the system temperature leads to increase of the process current efficiency until it reaches the asymptotically leveling effect in the system temperature ranging about 65 oC.

3. A highest current efficiency (about 91%) can be obtained in solution acidity of 6.1-6.3.
4. Increasing the electrolyte flow rate can bring a significant improvement to the process current efficiency, keeping in mind the limitation of the successful increasing of the electrolyte flow rate with regard to the effect of the reactor volume on the degree of the active chlorine conversion to the final product.

The current density is the important parameter affecting the current efficiency of the chlorate cell process. At a low current density, the oxidation of the chloride may not proceed any more, thus, an increasing in the anodic current density will lead to improve the current efficiency of the process successfully

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