

Studies on the Electrolytic Preparation of Ba(ClO₄)₂

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The electrochemical preparation of barium perchlorate, Ba(ClO₄)₂, from barium chlorate employing a platinum anode and a rotating stainless steel cathode is described. The effect of electrolyte concentration, cathode and anode current densities, pH and temperature of the electrolyte, and cathode rotation on current efficiency for the preparation of barium perchlorate was studied. A maximum current efficiency of 40% was achieved corresponding to an energy consumption of 5.5 kW·h·kg⁻¹.

Introduction

The preparation of alkali metal perchlorates by electrolysis of the corresponding chlorates has been studied by various authors.¹ Schumacher² reported other methods for manufacturing of perchlorates from different raw materials. The mechanism, kinetic aspects, and electrode materials for perchlorate formation were dealt with in the literature.^{3–7} After understanding the mechanism of perchlorate formation, attempts were made to study the different anode materials like platinum⁸ and lead dioxide.⁶ Regardless of the mechanism at the electrodes in a perchlorate cell it has been well-established that a high anodic potential is essential. To secure this high anodic potential, a platinum electrode is generally used. Earlier literature contains references to the use of platinum anodes.⁸ In spite of its high cost and the corrosion and erosion that takes place in a cell when it is used as an anode, platinum is still the material of choice for commercial cells. So in the present case, platinum is used as the anode material. However, Platinum-clad tantalum, platinum-coated tantalum, and platinum-coated titanium are future anode materials which would decrease the weight of platinum and thereby the cost.

The literature contains only one publication relating to the preparation of alkaline earth metal perchlorates by electrolysis, and this was the use of platinum electrodes by Ilin et al.⁹ In view of the scant literature on the electrochemical preparation of alkaline earth metal perchlorates, it is clear that the electrochemical route was considered inappropriate for alkaline earth metal perchlorates, due to precipitation of the corresponding metal hydroxides, which have poor solubility vs the hydroxides of alkali metals. The authors were successful in preparing magnesium and barium chlorate^{10–13} where metal-oxide-coated titanium was used as the anode and a rotating cathode was employed to minimize the precipitation of the corresponding metal hydroxides.

Therefore, the main objective of this study is to prepare barium perchlorate from barium chlorate, by an electrochemical method, using platinum and rotating stainless steel as the anode and cathode, respectively. To optimize the parametric conditions, various parameters like the effects of electrolyte concentration, pH and temperature, current density, and cathode rotation on current efficiency were investigated.

Barium perchlorate is used as a dehydrating agent and ammonia absorbent. It is also used for preparing perchloric acid.

Materials and Methods

Cell Construction and Electrolysis. The electrolytic cell consisted of a 0.5-L glass vessel fitted with a PVC cell cover with slots to introduce the electrodes, a pH sensor, a thermometer, and electrolytes. Cylindrical stainless steel (SS304 of purity 99.8%; SAIL, India) rods of different dimensions [0.010 m (diameter) × 0.08 m (height), 0.015 m (diameter) × 0.07 m (height), and 0.025 m (diameter) × 0.09 m (height)] were used as cathodes. Depending on the parameters, each cathode was fitted to a rotating assembly and positioned at the center of the cell at an interelectrode distance of 1.0 cm. A platinum foil of size 0.025 m (breadth) × 0.085 mm (length) was used as the anode. The electrolytic cell was placed in a thermostat, and the temperature of the electrolyte was maintained with a variation of ±1 K. The barium chlorate solution obtained from the electrolysis of barium chloride was used as the electrolyte.¹³

The electrical connection to the cathode was through the mercury contained in a cup attached to the top end of the rotating shaft driven by a 0.5-hp motor. Regulated direct current (dc) was supplied from a rectifier (25 A, 0–25 V, Aplab Model). A 0.45-L portion of solution was used for each experiment; this was the electrolyte. The electrolyte pH was monitored using a pH probe and regulated by adding either acid or base. Each experiment was continued until the theoretical charge had been passed. All the experiments were carried out three times for reproducibility. The cumulative current efficiency was calculated for each experiment. The effect of various parameters on current efficiency was determined.

Analysis

Chloride. Chloride was estimated using 0.1 N silver nitrate (analar grade; Ranbaxy, India) and 1% K₂CrO₄ (analar grade; Ranbaxy, India).¹⁴

Chlorate. Chlorate was estimated iodometrically using 0.1 N thiosulfate in the presence of KBr (3.0 g), conc. HCl (30 mL), and 10% KI (10 mL).¹⁵

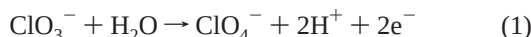
Perchlorate. Perchlorate was estimated using a perchlorate ion-selective electrode (Elico, India).

Barium. Barium was determined by titration with 0.1 N EDTA (analar grade; BDH, India) at pH 10 using Solochrome Black-T (analar grade; BDH, India) as an indicator.¹⁶

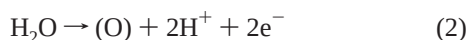
Results and Discussion

Chlorate is oxidized to perchlorate according to the following overall reaction:

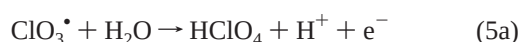
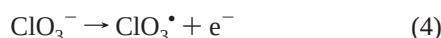
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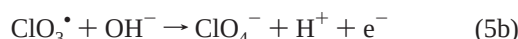
Although several mechanisms have been proposed,^{3,5–7} two mechanisms for the anodic oxidation of chlorate are worth discussion. According to the first mechanism, the chlorate reacts with discharged oxygen resulting from the oxidation of water and chemisorbed at the electrode surface.¹⁷



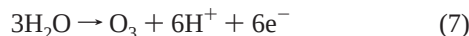
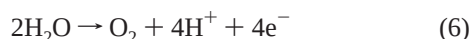
According to the second mechanism, the primary step is the direct discharge of the chlorate ion at the anode with the formation of free chlorate radical, which then reacts with water to form perchlorate.^{5,6}



However, under alkaline conditions, the formation of perchlorate may takes place as follows:¹⁸



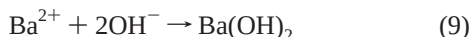
Apart from the above reactions, competing reactions are the formation of oxygen and ozone (especially toward the last stages of chlorate conversion).



In addition to the loss reactions (eqs 6 and 7), an additional retarding cathodic reaction, by way of precipitation of metal hydroxides due to their lower solubilities as indicated below, will also be encountered in the case of alkaline earth metal prechlorates.



According to the Ba^{2+} – H_2O Pourbaix diagram,¹⁹ barium hydroxide formation is predicted by the following reaction



The barium hydroxide forms an adherent coating over the cathode in the pH range of 12.5–14.0. Barium ions, such as $\text{Ba}(\text{OH})_2$ ($K_{\text{sp}} = 5 \times 10^{-3}$), can protect the metal surface and hinder further reaction. The precipitation of this metal hydroxide depends on factors such as electrolyte concentration, pH, temperature, current density, and cathode rotation.

The standard potentials of reactions 1 and 6 are close so that oxygen evolution is always an accompanying reaction, i.e., chlorate oxidation and oxygen evolution take place at the anode with complimentary current efficiencies. Furthermore, the influence of pH on the equilibrium potentials for both reactions 1 and 6 is the same¹⁷ so that these two reactions can occur simultaneously, irrespective of the pH. This situation is altered in the presence of high concentrations of chlorate, as well as increased anode current densities as reported by De Nora et al.⁵ According to De Nora, the anodic polarization on platinum and lead dioxide is strongly influenced by the presence of ClO_3^- ions, on account of their progressive adsorption at the interface

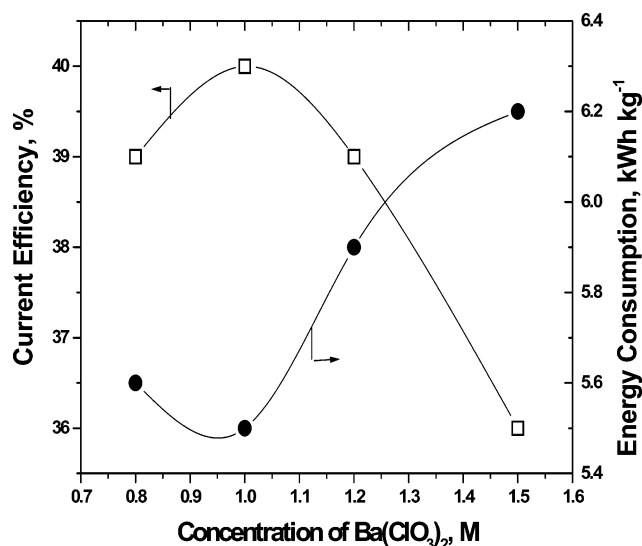


Figure 1. Variation of current efficiency and energy consumption with concentration: (conditions) electrolyte pH 6.0; electrolyte temperature 333 ± 2 K; anodic current density $30.0 \text{ A}\cdot\text{dm}^{-2}$; cathode current density $32.0 \text{ A}\cdot\text{dm}^{-2}$; cathode peripheral velocity $1.38 \text{ m}\cdot\text{s}^{-1}$.

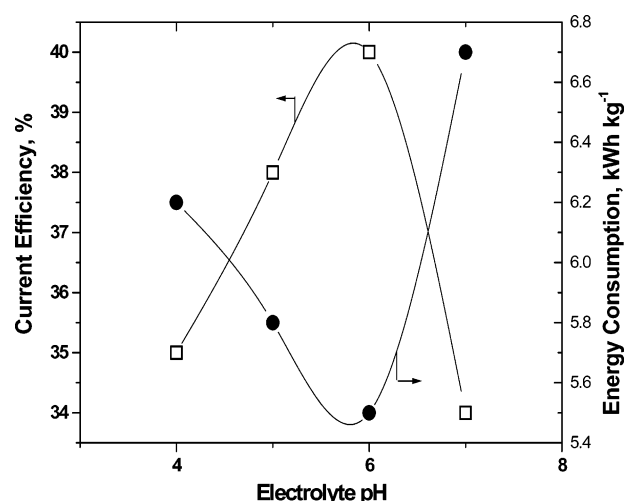


Figure 2. Variation of current efficiency and energy consumption with electrolyte pH: (conditions) electrolyte concentration 1.0 M ; electrolyte temperature 333 ± 2 K; anodic current density $30.0 \text{ A}\cdot\text{dm}^{-2}$; cathode current density $32.0 \text{ A}\cdot\text{dm}^{-2}$; cathode peripheral velocity $1.38 \text{ m}\cdot\text{s}^{-1}$; theoretical quantity of charge passed $43.0 \text{ A}\cdot\text{h}$.

Table 1. Effect of the Temperature of the Electrolyte on Current Efficiency for the Preparation of Barium Perchlorate^a

S. no.	electrolyte temp ± 1 K	final conc (M)		current efficiency for $\text{Ba}(\text{ClO}_4)_2$ formation	energy consumption for $\text{Ba}(\text{ClO}_4)_2$ formation ($\text{kW}\cdot\text{h}\cdot\text{kg}^{-1}$)
		chlorate	perchlorate		
1	323	0.49	0.38	38	5.9
2	333	0.46	0.40	40	5.5
3	343	0.46	0.41	41	4.8
4	353	0.36	0.44	42	4.4

^a Conditions: electrolyte concentration 1.0 M ; electrolyte pH 6.00; anode current density $30.0 \text{ A}\cdot\text{dm}^{-2}$; cathode current density $32.0 \text{ A}\cdot\text{dm}^{-2}$; cathode peripheral velocity $1.38 \text{ m}\cdot\text{s}^{-1}$; theoretical quantity of charge passed $43.0 \text{ A}\cdot\text{h}$.

as electrostatic attraction increases with potential. Consequently, the water molecules adsorbed at the interface are gradually displaced by ClO_3^- ions, which thus hinder the primary discharge of water and consequently oxygen evolution. This is evidenced, in particular, by the strong inflection generally

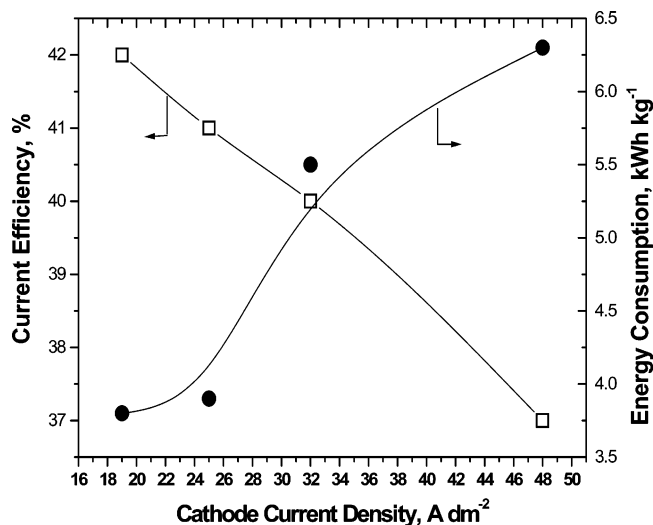


Figure 3. Variation of current efficiency and energy consumption with cathode current density: (conditions) electrolyte concentration 1.0 M; electrolyte pH 6.0; electrolyte temperature 333 ± 2 K; anodic current density $30.0 \text{ A} \cdot \text{dm}^{-2}$; cathode peripheral velocity $1.38 \text{ m} \cdot \text{s}^{-1}$; theoretical quantity of charge passed $43.0 \text{ A} \cdot \text{h}$.

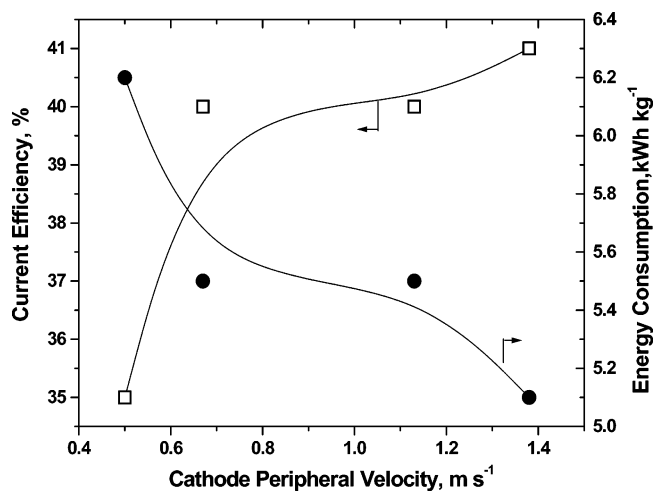


Figure 4. Variation of current efficiency and energy consumption with cathode peripheral velocity: (conditions) electrolyte concentration 1.0 M; electrolyte pH 6.0; electrolyte temperature 333 ± 2 K; anodic current density $30.0 \text{ A} \cdot \text{dm}^{-2}$; cathode current density $32.0 \text{ A} \cdot \text{dm}^{-2}$; theoretical quantity of charge passed $43.0 \text{ A} \cdot \text{h}$.

observed on platinum at all concentrations and also lead dioxide in the lower concentration range.⁷ However, this does not provide by itself any evidence in favor of the mechanism of primary ClO_3^- discharge, besides water displacement from the double layer as postulated above. A further possibility may in particular be visualized that the active sites of high oxygen adsorption energy are progressively blocked by the adsorbed chlorate ions, with a consequent modification of the oxide film and a rise in oxygen discharge overpotential. This could allow the adsorbed chlorate ions to react with oxygen in the modified oxide film, so that chlorate oxidation would occur as a secondary reaction with the chemisorbed oxygen atoms resulting from the primary discharge of water. As a result, an increase in chlorate concentration enhances the chlorate conversion rate. On the other hand, oxygen evolution is strongly inhibited by the adsorbed chlorate ions and depends on the amount of ClO_3^- ions also in the concentration range throughout which the relevant polarization curve remains unaffected. That is, higher concentrations of chlorate inhibit oxygen evolution because of preferential adsorption of chlorate and thereby increase the current ef-

Table 2. Effect of Anode Current Density on Current Efficiency for the Preparation of Barium Perchlorate^a

S. no.	anode current density ($\text{A} \cdot \text{dm}^{-2}$)	final conc (M)		current efficiency for $\text{Ba}(\text{ClO}_4)_2$ formation	energy consumption for $\text{Ba}(\text{ClO}_4)_2$ formation ($\text{kW} \cdot \text{h} \cdot \text{kg}^{-1}$)
		chlorate	perchlorate		
1	18	0.52	0.36	35	5.2
2	24	0.50	0.37	37	5.6
3	30	0.46	0.40	40	5.5
4	37	0.30	0.46	43	5.2

^a Conditions: electrolyte concentration 1.0 M; electrolyte pH 6.00; electrolyte temperature 333 K; cathode current density $32.0 \text{ A} \cdot \text{dm}^{-2}$; cathode peripheral velocity $1.38 \text{ m} \cdot \text{s}^{-1}$; theoretical quantity of charge passed $43.0 \text{ A} \cdot \text{h}$.

Table 3. Results of the 50-A Cell for the Production of Barium Perchlorate

operating parameters	results
1. electrolyte	$\text{Ba}(\text{ClO}_3)_2$
2. volume of electrolyte	8.5 L
3. initial concentration	
ClO_3^-	1.0 M
ClO_4^-	0.0 M
4. electrolyte pH	6.0
5. electrolyte temperature	333 ± 2 K
6. final concentration	
ClO_3^-	0.46 M
ClO_4^-	0.40 M
7. current passed	50 A
8. anode current density	$30.0 \text{ A} \cdot \text{dm}^{-2}$
9. cathode current density	$32.0 \text{ A} \cdot \text{dm}^{-2}$
10. cathode peripheral velocity	$1.38 \text{ m} \cdot \text{s}^{-1}$
11. average voltage	6.9 V
12. current efficiency	40.0%
13. energy consumption	$5.5 \text{ kW} \cdot \text{h} \cdot \text{kg}^{-1}$

iciency. The opposing trend with barium chlorate electrolysis must be connected with the removal of barium as its hydroxide with the corresponding anodic evolution of oxygen. It is found²⁰ that the $\text{pH}_{(\text{s})}$ increases with an increasing Mg^{2+} concentration. Similarly on the basis of what has been said above, in this case also, it may be assumed that a sparingly soluble hydroxide is formed in the layer next to the cathode. In the present instance, with higher concentrations of electrolyte, the $\text{pH}_{(\text{s})}$ can easily become alkaline, resulting in the precipitation of $\text{Ba}(\text{OH})_2$ and deposition on the cathode surface. The loss of Ba^{2+} as $\text{Ba}(\text{OH})_2$ increases 0.04–0.06 M when the concentration of barium chlorate increases from 1.0 to 1.5 M, and consequently, the current efficiency decreases from 40 to 36%. Figure 1 shows the variation of current efficiency and energy consumption with concentration for the formation of barium perchlorate.

The formation of perchlorate is not dependent on the pH of the electrolyte within the specified range say around 6.0,⁷ but when the solution is made alkaline, the current efficiency falls rapidly, a fact which is explained³ due to the discharge potential for oxygen at platinum being lower in alkaline than in acid solutions. Furthermore, the oxidizing power is lower in alkaline than in neutral or acid solutions. This is to be concluded from the fact that many oxidations, which take place readily in acid solutions, are either entirely prevented or proceed at a very much decreased rate when the solution is made alkaline. It is noted that at the time of starting the electrolysis both the potential of the anode and the efficiency are somewhat below their normal values.⁸ Both, however, steadily increase to a maximum after a certain duration of time. This is entirely to be expected from the fact that reliable measurements of anode overpotential always indicate a low concentration of active oxygen during the first few moments of oxygen discharge.¹⁷ It is also reported¹⁷ that if the solution is made alkaline at the anode the efficiency

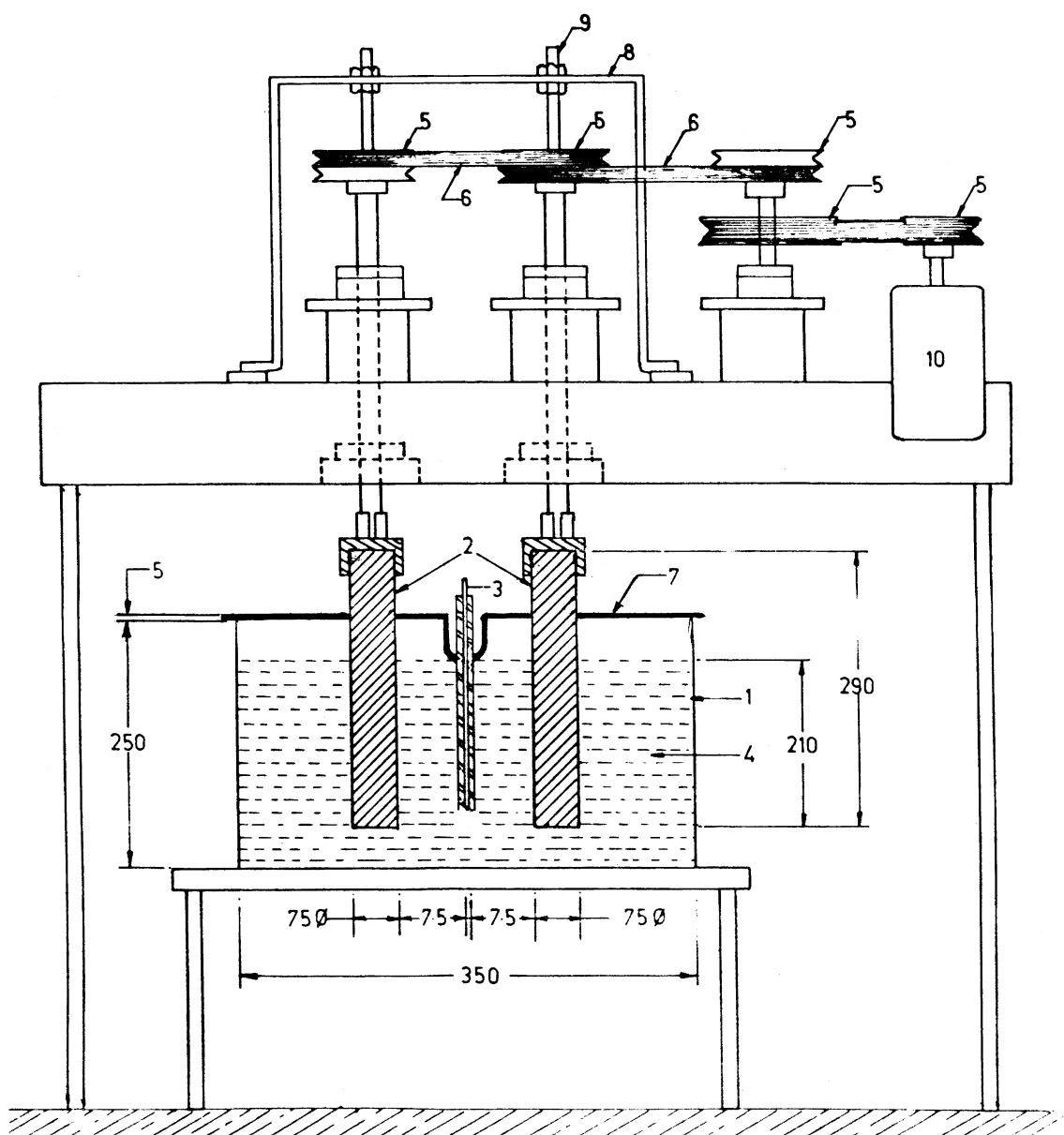
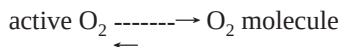


Figure 5. Sketch of a 50-A cell: (1) stainless steel tank, (2) stainless steel cathode, (3) anode, (4) electrolyte, (5) pulleys, (6) V-belts, (7) PVC cover, (8) copper bus bar, (9) mercury cup, and (10) 0.5-hp motor.

of perchlorate production falls off rapidly, a fact which is explained by the increased ease of oxygen discharge in a solution containing a high concentration of hydroxyl ion. The result is the discharge of oxygen along with the chlorate ions and consequent drop in the anode efficiency. This hypothesis best explains the rise from a comparatively low efficiency at the beginning of the electrolysis to a higher value as the electrolysis proceeds. When the oxidation is taking place at a high efficiency and the current is interrupted for a short time, it is found, upon closing the circuit, that the efficiency is low just as it has been during the first few minutes of the experiment. The idea is that during the break in the current flow the concentration of free chloric acid at the anode falls,¹ largely through diffusion, and that a certain length of time is necessary for the chloric acid to accumulate to that concentration in which it is unstable.¹⁷ During this time, oxygen is evolved and efficiency necessarily falls. Figure 2 shows the variation of current efficiency with energy consumption for different pHs of the electrolyte for the preparation of barium perchlorate. At pH 4.0, the current

efficiency is less than that at pH 6.0. This is expected, because at lower pH values the evolution of chlorine gas can take place.¹¹ If the pH is higher than 6.0, say 7.0, it is expected that the pH of the layer adjacent to the cathode becomes more alkaline, thereby favoring the precipitation of metal (Ba^{2+}) hydroxide and also resulting in the ease of oxygen discharge from a solution containing a high concentration of OH^- ions and consequently reduction in current efficiency for the preparation of perchlorate.

Earlier workers have ascribed the effect of temperature on perchlorate formation to various factors. It is reported that²¹ the decrease in perchlorate formation caused by the increase of temperature at a given current density may be due to the increase in the concentration of OH^- ions caused by the increased dissociation of water at higher temperatures. Bennett and Mack¹⁷ state that an increase in electrolyte temperature decreases the current efficiency markedly since the concentration of active oxygen present at the anode at any given time is dependent upon the state of the equilibrium.



Increased temperature tends to shift this equilibrium in favor of molecular oxygen, and therefore, a lower active oxygen concentration and consequently a lower oxidation power can be expected. A sufficiently higher current density at high temperature would, however, tend to increase the rate of production of active oxygen and increase its concentration at the electrode. With the increase of current density, it can, therefore, be expected that a rise in the efficiency of chlorate oxidation will be obtained thereby overcoming the inhibiting effect of high temperature. This is actually realized experimentally.²¹ In the present instance at higher current densities, it is expected that better current efficiency with increasing temperature will be achieved, which has been realized experimentally. At the anode current density of $24 \text{ A}\cdot\text{dm}^{-2}$, the current efficiency has been found to be 37% for barium perchlorate by maintaining the temperature of 333 K. This was raised to 43% at $37 \text{ A}\cdot\text{dm}^{-2}$, the temperature remaining constant at 333 K. Table 1 shows the effect of the temperature of the electrolyte on current efficiency for the preparation of barium perchlorate. In the present case, the rise in temperature increases the current efficiency up to the temperature studies. This higher current efficiency with the increase of temperature can also be attributed to the higher solubility of barium hydroxide at higher temperatures,²² in addition to what has been discussed above.

In the oxidation of sodium chlorate at a platinum anode, the anodic polarization curves have been divided into partial curves for the two reactions, namely, chlorate oxidation and oxygen evolution.¹ It has been found that, at higher anodic current densities, the increase of partial current density with overpotential is faster for perchlorate formation than for oxygen evolution. In other words, at higher current densities, oxygen evolution (reaction 6) is inhibited and, thereby, increases the formation efficiency of perchlorate (reaction 1). This is also true for the electrolysis of barium chlorate as shown in Table 2.

It is found that,^{23,24} $\text{pH}_{(\text{s})}$ is increased by increasing the cathode current density and favoring the hydroxide formation. The results in the present instance confirm the same finding. In the present study, it is, visually, found that the loss of Ba^{2+} as barium hydroxide increases with increasing cathode current density, thereby resulting in the lowering of current efficiency. Figure 3 shows the effect of cathode current density on the current efficiency for the preparation of barium perchlorate.

Even in the absence of mechanical agitation, the cathode surface layer is continuously disturbed due to hydrogen evolution, so that the $\text{pH}_{(\text{s})}$ will change only gradually. In the present case, the gas evolution is insufficient to maintain the $\text{pH}_{(\text{s})}$ at the pH value of 6. To achieve such pH control, the cathode has to be rotated. It has been found in our earlier studies on the formation of magnesium chlorate also^{10,25} that increasing the peripheral velocity will produce the desired value of $\text{pH}_{(\text{s})}$ vs that with slower rotation. Figure 4 shows that the current efficiency increases with cathode rotation and it is maximum at a peripheral velocity of $1.38 \text{ m}\cdot\text{s}^{-1}$. This is due to the effective removal of OH^- ions at the cathode by consequently minimizing the precipitation of barium hydroxide.

From the above results, it is found that the maximum current efficiency of 40% with an energy consumption of $5.5 \text{ kW}\cdot\text{h}\cdot\text{kg}^{-1}$ was achieved, when $1.0 \text{ M Ba}(\text{ClO}_3)_2$ (pH 6.0) is electrolyzed under the following parameters: an anode current density of $30.0 \text{ A}\cdot\text{dm}^{-2}$, a cathode current density of $32 \text{ A}\cdot\text{dm}^{-2}$, a

temperature of 333 K, and with a cathode peripheral velocity of $1.38 \text{ m}\cdot\text{s}^{-1}$.

50-A Bench Scale Experiments. On the basis of results obtained on the laboratory scale, a 50-A cell was designed, fabricated, and operated for the electrolytic preparation of barium perchlorate. A stainless steel tank [0.35 m (length) $\times$ 0.25 m (width) $\times$ 0.25 m (height)] was fitted with a poly(vinyl chloride) (PVC) cover having suitable holes to introduce the anode, cathode, thermometer, and electrolyte and acted as the cell. A platinum anode [0.17 m (width) $\times$ 0.18 m (height)] was used. Two cylindrical stainless steel tubes [0.075 m (diameter) $\times$ 0.21 m (height)] closed at the bottom and fitted to the rotating assemblies acted as the cathode and were positioned on either side of the anode with an interelectrode distance of 1 cm. Figure 5 shows a sketch of the cell. The electrical connection to the cathode was given through mercury contained in a cup attached to the top end of the rotating shaft. Regulated direct current (dc) was supplied from a rectifier (0–25 V, 100 A). The electrolysis was carried out with $1.0 \text{ M Ba}(\text{ClO}_3)_2$ (pH 6.0), at an anode current density of $30.0 \text{ A}\cdot\text{dm}^{-2}$ and a cathode current density of $32.0 \text{ A}\cdot\text{dm}^{-2}$ with a temperature of 333 K. The cathode peripheral velocity was maintained at $1.38 \text{ m}\cdot\text{s}^{-1}$. The current efficiency obtained in the 50-A cell (Table 3) conforms well to the results obtained at laboratory scale.

Conclusion

The electrochemical oxidation of barium chlorate to perchlorate can proceed with efficiency, when $1.0 \text{ M Ba}(\text{ClO}_3)_2$ (pH 6.0) is electrolyzed using a platinum anode and stainless steel cathode with anode current densities of $30 \text{ A}\cdot\text{dm}^{-2}$, a cathode current density of $32 \text{ A}\cdot\text{dm}^{-2}$, a temperature of 333 K, and an anode peripheral velocity of $1.38 \text{ m}\cdot\text{s}^{-1}$ to achieve a current efficiency of 40% corresponding to an energy consumption of $5.5 \text{ kW}\cdot\text{h}\cdot\text{kg}^{-1}$.

Acknowledgment

The authors wish to express their gratitude to the Director, Central Electrochemical Research Institute, Karaikudi, for permission to publish this paper.

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Received for review April 1, 2007

Revised manuscript received July 8, 2007

Accepted July 13, 2007

IE070466R