

Electrochemical Preparation of Barium Chlorate from Barium Chloride

Subramanyan Vasudevan* and Swaminathan Mohan

Central Electrochemical Research Institute (CSIR), Karaikudi 630 006, India

The electrochemical oxidation of barium chloride to chlorate employing a noble metal oxide coated anode and a rotating stainless steel cathode is described. The effect of different electrolyte concentration, anode and cathode current density, pH and temperature of the electrolyte, and cathode rotation on current efficiency for the preparation of barium chlorate was studied. A maximum current efficiency of 56% was achieved corresponding to the energy consumption of $7.1 \text{ kW}\cdot\text{h}\cdot\text{kg}^{-1}$.

Introduction

The preparation of alkali metal chlorates by electrolysis of the corresponding chlorides has been studied by various authors.¹ The mass transport, mechanism, and kinetic aspects for chlorate formation were dealt with in the literature.^{2–8} After understanding the mechanism of chlorate formation, attempts were made to study different anode materials such as graphite, magnetite, lead dioxide, and noble metal oxides. Graphite undergoes considerable wear due to the oxidation of the binder material^{9,10} resulting in the formation of carbon dioxide. Due to its disintegration, it not only contaminates the chloride electrolyte but also increases the interelectrode distance during electrolysis, thereby increasing the cell voltage and, consequently, the energy consumption. Several authors have studied, in detail, the influence of different parameters^{11–15} on the consumption of graphite.

Magnetite was another anode material industrially used in chloride oxidation.¹⁶ In this case, wear is moderate and the anode was dimensionally stable during electrolysis and stable at higher temperatures unlike graphite. The disadvantage of this material is low conductivity and high fragility. Lead dioxide was one another anode material studied for chloride oxidation^{17,18} since it has a higher conductivity than most of the metal oxides. The disadvantages of this electrode are poor electrocatalytic action and higher overvoltage for chlorine evolution. Due to the above disadvantages of the graphite, magnetite, and lead dioxide anodes, noble metal oxide coated titanium anodes are being substituted. The advantage and important features of these are low chlorine overvoltage, higher electronic conductivity, and high chemical stability.

The literature contains no publication dealing with investigations on the production of alkaline earth metal chlorates by the electrolysis of chlorides at noble metal oxide electrodes, and the only publication that relates to the preparation of alkaline earth metal chlorates by electrolysis was that on the use of platinum electrodes by Ilin et al.¹⁹ In view of the scant literature on the electrochemical preparation of alkaline earth metal chlorates, it is clear that the electrochemical route was considered inappropriate for alkaline earth metal chlorates, due to precipitation of the corresponding metal hydroxides, which have poor solubility compared to the hydroxides of alkali metals. The authors were successful in preparing magnesium, strontium chlorates, and perchlorates by electrochemical oxidation,^{20–23} where the rotating cathode was employed to minimize the

precipitation of hydroxides. Now, an attempt has been made to prepare barium chlorate using a noble metal oxide coated anode and a rotating stainless steel cathode and the results are presented in this paper.

Materials and Methods

Cell Construction and Electrolysis. The electrolytic cell (Figure 1) consisted of a 0.5-L glass vessel fitted with a PVC cell cover with slots to introduce the electrodes, pH sensor, thermometer, and electrolytes. Cylindrical stainless steel (SS304 of purity 99.8%; SAIL, India) rods of different dimensions [0.010 m (diameter) \times 0.08 m (height), 0.015 m (diameter) \times 0.07 m (height), and 0.025 m (diameter) \times 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. Noble metal oxide ($\text{RuO}_2/\text{TiO}_2/\text{SnO}_2$) coated titanium mesh (0.006 m^2) of 99.8% purity (Mithani (I) Limited, India) surrounding the cathode acted as the anode with an interelectrode distance of 1.0 cm. The mixed oxide electrodes were prepared by the thermal decomposition process as described in the literature.²⁴ The coating solution for the preparation of the anodes was prepared from the chlorides of the three metals, viz., $\text{RuCl}_3\cdot x\text{H}_2\text{O}$ (38.4% Ru; Johnson Mathey, UK), TiCl_4 (25.1% Ti; Riedel De Haan AG), and $\text{SnCl}_4\cdot 5\text{H}_2\text{O}$ (33.9% Sn; J.T. Baker Chemical Co., USA). The salts of the above three metals were taken in the ratio of 30 $\text{RuO}_2/50 \text{ TiO}_2/20 \text{ SnO}_2$, dissolved in 2-propanol (Johnson Mathey, UK), and then painted over the pretreated titanium mesh (which was polished, degreased, and etched in 10% oxalic acid (Johnson Mathey, UK) solution at 363 K for 30 min) to produce a uniformly spread layer. The paint layer was dried at 353 K in an air oven for 10 min to evaporate the solvent. The samples were then transferred to a muffle furnace kept at 673 K for 10 min. During this period, the heating zone of the furnace was maintained with a good supply of air from a compressor. The electrode was then removed from the furnace and cooled. The process of brushing the coating solution, drying at 353 K, and then heating in the presence of air at 673 K was repeated 6–8 times. After the final coating, the electrode was heated at 723 K for 1 h and allowed to cool in the oven itself over a period of 8 h.

Electrical connection to the cathode was through mercury contained in a cup attached to the top end of the rotating shaft driven by a 0.5-hp motor. Regulated direct current was supplied from a rectifier (25 A, 0–25 V, Aplab model).

Barium chloride (Laboratory Reagent) was dissolved in distilled water for the required concentration; A 0.45 L portion of solution was used for each experiment, which was used as the electrolyte. The electrolyte pH was monitored using a pH

* To whom correspondence should be addressed. Phone: 91 4565 227554. Fax: 91 4565 227779. E-mail: vasudevan65@gmail.com and svdevan_2000@yahoo.com.

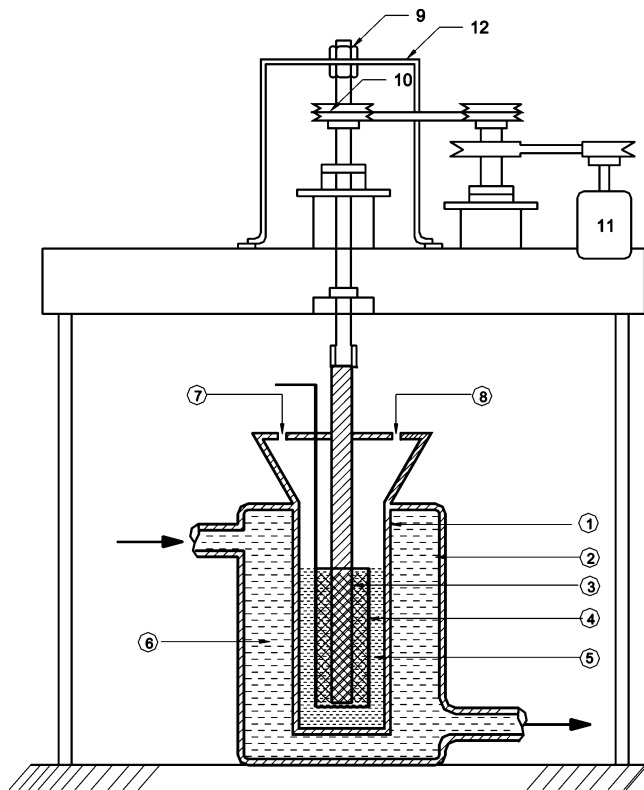


Figure 1. Laboratory scale cell assembly: (1) cell, (2) thermostat, (3) stainless steel cathode, (4) anode, (5) electrolyte, (6) thermostatic water, (7 and 8) holes to introduce pH sensor and thermometer, (9) mercury cup, (10) pulleys, (11) 0.5-hp motor, and (12) copper bus bar.

probe and regulated by adding either acid or base. Each experiment was continued until the theoretical charge had been passed, and 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 a standard silver nitrate (analar grade, Ranbaxy, India) solution and fluorescein (analar grade, BDH, India) as an indicator.²⁵

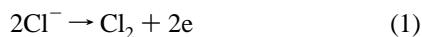
Chlorate. Chlorate was estimated iodometrically.²⁶

Barium. Barium was determined by titration with EDTA (analar grade, BDH, India) at pH 10 using solochrome black-T (analar grade, BDH, India) as an indicator.²⁷

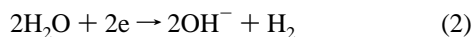
Results and Discussion

During the electrolytic oxidation of a chloride solution to obtain chlorate, the primary products of the electrode reactions are chlorine and alkali, which react in the bulk electrolyte between the electrodes to form hypochlorous acid and hypochlorite. These are subsequently reacting chemically to form chlorate.¹

The main reactions in the chlorate electrolysis process can thus be written as follows. At the anode, chlorine is formed.

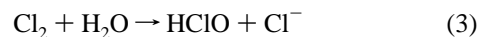


At the cathode, hydroxyl ions and hydrogen are formed.

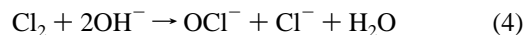


In the bulk, chlorine ions formed at the anode react rapidly with

water to form hypochlorous acid.

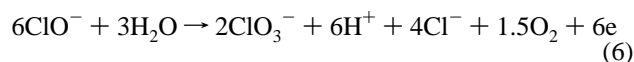
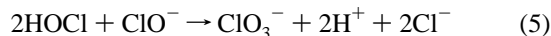


Since the electrodes are close together and have no diaphragm, the chlorine can react with hydroxyl ions formed at the cathode to produce hypochlorite ions.



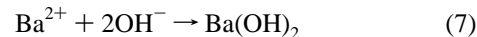
As a result, the solution around the anode becomes strongly acidic and the solution in contact with the cathode is alkaline. In addition to this pH gradient, the concentration of hypochlorous acid also establishes a gradient relatively high around the anode and relatively low around the cathode.

It is usually assumed that chlorate is formed by the reaction of hypochlorite ion by free hypochlorous acid (reaction 5) when the pH is 6.0–6.5. However, when the pH is slightly alkaline, the electrochemical formation of chlorate through discharge of the hypochlorite



ion occurs at a potential equal to that for discharge of the chloride ion (reaction 6).

According to reactions 5 and 6, chlorate may be formed in two ways: either by a purely chemical reaction of the hypochlorite ion with hypochlorous acid in the bulk solution (chemical chlorate formation) or by electrochemical oxidation of the hypochlorite at the anode under simultaneous oxygen evolution (anodic chlorate formation). If all chlorate is formed by chemical reaction 5, 12 Faradays are consumed in the oxidation of 1 mol of chloride to chlorate. This is said to correspond to a maximum current efficiency of 100%. If all chlorate is formed by reaction 6, the current efficiency cannot be higher than 66.5% since one-third of the current is used for the evolution of oxygen. In other words, reaction 6 can be considered to be an anodic loss reaction. It has been established that reaction 5 is more plausible than reaction 6.¹ The most favorable operating conditions for reaction 5 are a temperature of 333–348 K with a pH of 6.0–6.5. The conditions for the formation of chlorate through reaction 5 exist in the present case also. Under these conditions, in the case of alkaline earth metal cations, an additional cathodic loss reaction, viz., the precipitation of a metal hydroxide, will be encountered due to their low solubility. According to the Ba–H₂O Pourbaix diagram,²⁸ barium hydroxide formation is predicted by the following reaction



$$\log [\text{Ba}^{2+}] = \log K - 2 \text{pH}$$

The barium hydroxide forms an adherent coating over the cathode in the pH range 12.5–14.0. Barium ions as Ba(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.

Effect of Initial Barium Chloride Concentration. The results for different initial concentrations of barium chloride ranging from 0.8 to 1.5 M and maintaining other parameters constant are given in Table 1. The current efficiency for the

Table 1. Effect of Initial Concentration of Barium Chloride on Current Efficiency for the Preparation of Barium Chlorate^a

s. no.	electrolyte conc (M)	theoretical charge passed (A·h)	voltage (V)	final concentration (M)		current efficiency for Ba(ClO ₃) ₂ formation (%)	energy consumption for Ba(ClO ₃) ₂ formation (kW·h·kg ⁻¹)
				chloride	chlorate		
1	0.8	125.0	3.8	0.47	0.46	51.0	7.90
2	1.0	140.0	3.8	0.50	0.51	51.0	7.90
3	1.3	193.0	3.8	0.68	0.56	45.0	10.00
4	1.5	204.0	4.0	0.58	0.58	39.0	10.90

^a Conditions: (electrolyte pH) 6.00; (electrolyte temperature) 333 ± 2 K; (anodic current density) 15.0 A·dm⁻²; (cathode current density) 14.0 A·dm⁻²; (cathode peripheral velocity) 0.67 m·s⁻¹.

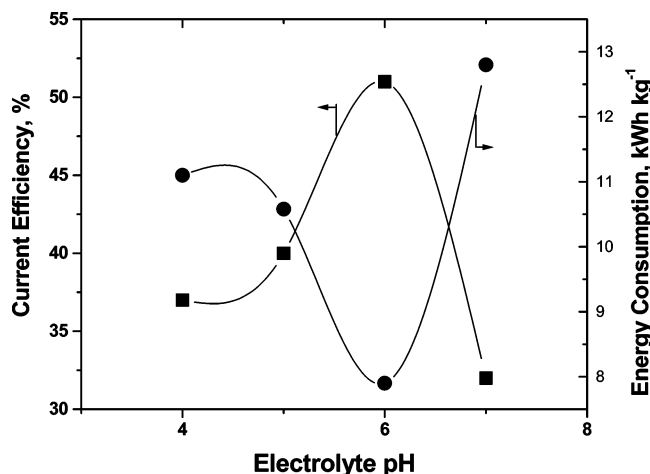


Figure 2. Variation of current efficiency and energy consumption with electrolyte pH, under the following conditions: (electrolyte concentration) 1.0 M; (electrolyte temperature) 333 ± 2 K; (anodic current density) 15.0 A·dm⁻²; (cathode current density) 14.0 A·dm⁻²; (cathode peripheral velocity) 0.67 m·s⁻¹; (theoretical quantity of charge passed) 140.0 A·h.

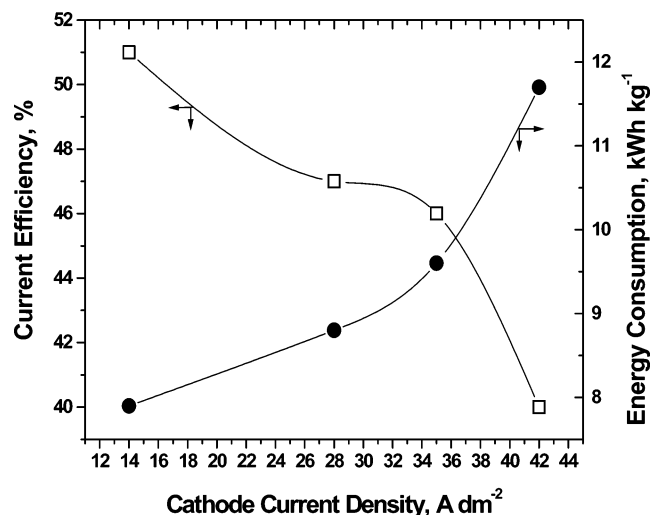


Figure 3. Variation of current efficiency and energy consumption with cathode current density, under the following conditions: (electrolyte concentration) 1.0 M; (electrolyte pH) 6.0; (electrolyte temperature) 333 ± 2 K; (anodic current density) 15.0 A·dm⁻²; (cathode peripheral velocity) 0.67 m·s⁻¹; (theoretical quantity of charge passed) 140.0 A·h.

formation of chlorate decreased with increasing concentration and was its maximum at 1.0 M; beyond this, it decreased. This is because, at higher concentrations of barium chloride, the precipitation of barium hydroxide is increased, thereby reducing the current efficiency.

Effect of pH and Cathode Current Density. Figures 2 and 3 show the effect of electrolyte pH and cathode current density, respectively, on current efficiency for the formation of barium chlorate. Unlike the alkali metal chloride reaction, the pH of the electrolyte and the cathode current density play significant

roles in determining the current efficiency of chlorate formation as they are directly connected with hydroxide formation.

Attempts have been made to measure the cathode surface pH, pH_(s), adopting different methods by various authors.²⁹ According to Kudrayavstev et al.,³⁰ in the case of KCl solution, the pH_(s) is accelerated by increasing the current density with an initial pH of 4.8 near the platinum electrode; the pH was increased to 5.9 and 14 at a current density of 0.1 and 100 A·m⁻², respectively. At still higher current densities, the increase in pH_(s) is higher still. In the present instance, with higher current densities, the pH_(s) can easily become alkaline (≥ 14), resulting in the precipitation of metal hydroxide and also deposition of the same on the cathode surface thereby hindering further reaction. The results in the present instance confirm the same. Figure 3 shows the effect of cathode current density on current efficiency for the preparation of barium chlorate. It is also found that the loss of Ba²⁺ as barium hydroxide increases with increasing cathode current density, thereby resulting in the lowering of the current efficiency. Moreover, the change in surface pH, pH_(s) (ΔpH), is also related to the bulk pH, pH_(b), and the cathode current density. At lower current densities, ΔpH is not appreciable whereas at higher current densities the ΔpH increases significantly, even at the same pH_(b).²⁹

The formation of chlorate is dependent on the pH of the electrolyte within the specified range.^{20–23,31} But, it is found that if the solution is made more alkaline or acidic, the current efficiency falls off quickly.³¹ When the electrolysis of an aqueous solution of chloride is carried out, initially, the discharge of Cl₂ and OH⁻ ions takes place; each of them may be discharged to a greater or lesser degree depending on the electrolysis conditions. In an alkaline medium, there is a predominant discharge of hydroxyl ions, thereby favoring the formation of free oxygen, and in an acid medium, conditions are favorable for the liberation of gaseous chlorine by the discharge of chloride ions. In a medium close to neutral, there is a simultaneous, approximately equivalent discharge of OH⁻ and Cl⁻ ions, favoring the subsequent chemical steps for the formation of chlorate. Figure 2 shows the variation of current efficiency with different electrolyte pHs for the preparation of barium chlorate. From the figure, it is evident that the higher current efficiency is observed at a narrow range of pH values around 6.0. The results indicate that increasing the electrolyte pH from 5.0 to 6.0 increases the current efficiency from 40 to 51% for the preparation of barium chlorate. But, at pH 7.0, it can be expected that the pH of the layer adjacent to the cathode is more alkaline, thereby favoring the precipitation of barium hydroxide with a loss of current efficiency for chlorate formation. Below pH 5.0, a shift in the HOCl/OCl⁻ ratio to below 2:1 occurs, which is not ideal for the production of chlorate. The excess hypochlorite can either be decomposed or oxidized at the anode to produce oxygen/chlorine in the loss of current efficiency at lower pH values. From the results, it is evident that the loss of chlorine and hydroxide precipitation

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

s. no.	anode current density ($\text{A}\cdot\text{dm}^{-2}$)	voltage (V)	final concentration (M)		current efficiency for $\text{Ba}(\text{ClO}_3)_2$ formation (%)	energy consumption for $\text{Ba}(\text{ClO}_3)_2$ formation ($\text{kW}\cdot\text{h}\cdot\text{kg}^{-1}$)
			chloride	chlorate		
1	5.00	3.4	0.66	0.31	31.0	11.60
2	10.00	3.6	0.57	0.43	43.0	8.80
3	15.00	3.8	0.50	0.51	51.0	7.90
4	20.00	4.1	0.48	0.54	54.0	8.10

^a Conditions: (electrolyte concentration) 1.0 M; (electrolyte pH) 6.00; (electrolyte temperature) 333 ± 2 K; (cathode current density) $14.0 \text{ A}\cdot\text{dm}^{-2}$; (cathode peripheral velocity) $0.67 \text{ m}\cdot\text{s}^{-1}$; (theoretical quantity of charge passed) $140.0 \text{ A}\cdot\text{h}$; (total hours of current passed) 14 h.

Table 3. Effect of Electrolyte Temperature on Current Efficiency for the Preparation of Barium Chlorate^a

s.no.	electrolyte temperature (K)	voltage (V)	final concentration (M)		current efficiency for $\text{Ba}(\text{ClO}_3)_2$ formation (%)	energy consumption for $\text{Ba}(\text{ClO}_3)_2$ formation ($\text{kW}\cdot\text{h}\cdot\text{kg}^{-1}$)
			chloride	chlorate		
1	313 ± 2	4.3	0.58	0.32	32.0	14.30
2	323 ± 2	4.1	0.57	0.42	42.0	10.40
3	333 ± 2	3.8	0.50	0.51	51.0	7.90
4	343 ± 2	3.6	0.54	0.60	55.0	6.50

^a Conditions: (electrolyte concentration) 1.0 M; (electrolyte pH) 6.00; (anode current density) $15.0 \text{ A}\cdot\text{dm}^{-2}$; (cathode current density) $14.0 \text{ A}\cdot\text{dm}^{-2}$; (cathode peripheral velocity) $0.67 \text{ m}\cdot\text{s}^{-1}$; (theoretical quantity of charge passed) $140.0 \text{ A}\cdot\text{h}$; (total hours of current passed) 14 h.

increases at pH values lower or higher than the optimum value (i.e., pH 6.0).

Effect of Anode Current Density. The results of the influence of anode current density on current efficiency are shown in Table 2, which clearly indicates that the current efficiency increases with increasing anode current density. This is in conformity with results reported^{1,8,32} earlier. However, the IR drop increases linearly with the current density, resulting in an increase of cell voltage and consequently higher energy consumption. Hence, a compromise has to be arrived at in selecting the current density for further investigation. It was thus maintained at $15.0 \text{ A}\cdot\text{dm}^{-2}$ for subsequent experiments.

Effect of Temperature. The temperature effect of the chlorate producing system is confined by a certain number of kinetic parameters encompassed by the relationship for current efficiency.⁸ In addition, it is well-known that an increase of temperature decreases the cell voltage, thereby resulting in energy reduction. The most important effect of temperature for the process would be to increase the rate of the chemical conversion of the active chlorine. In the present case, from the economical point of view, a rather compromised temperature range of about 333 K can be maintained in the chlorate cells with a metal oxide coated titanium anode. Another important reason for limiting the temperature of the chlorate producing system is due to the thermal decomposition of the hypochlorous species resulting in oxygen evolution.

The result of the effect of temperature on the preparation of barium chlorate is presented in Table 3. It is clear from the table that the current efficiency for the formation of barium chlorate increases with the increasing temperature of the electrolyte. The current efficiency for the formation of barium chlorate increases from 32 to 55% for an increase in temperature from 313 to 343 K. This increase in current efficiency at higher temperatures is attributed not only to an increase in the rate of chemical conversion of the active chlorine to chlorate¹ but also to the higher solubility of barium hydroxide.³³

Effect of Cathode Rotation on Current Efficiency. 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 found³⁴ that increasing the peripheral velocity will

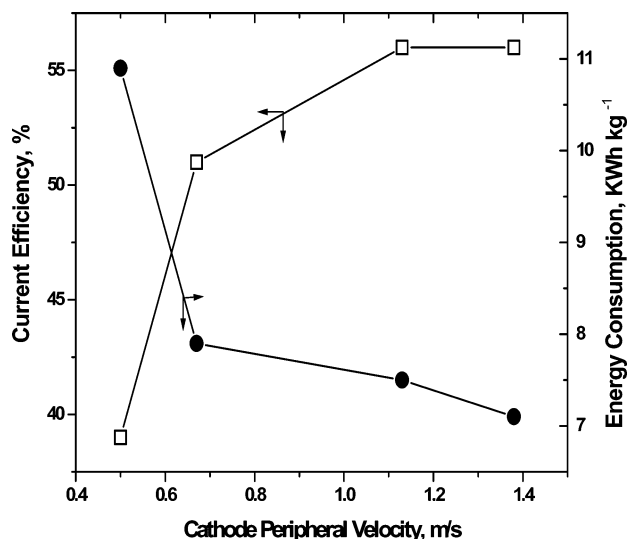


Figure 4. Variation of current efficiency and energy consumption with cathode peripheral velocity, under the following conditions: (electrolyte concentration) 1.0 M; (electrolyte pH) 6.0; (electrolyte temperature) 333 ± 2 K; (anodic current density) $15.0 \text{ A}\cdot\text{dm}^{-2}$; (cathode current density) $14.0 \text{ A}\cdot\text{dm}^{-2}$; (theoretical quantity of charge passed) $140.0 \text{ A}\cdot\text{h}$.

produce the desired value of $\text{pH}_{(\text{s})}$ as compared to that with slower rotation. Figure 4 shows that the current efficiency increases with cathode rotation and that its maximum is 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 51% was achieved when 1.0 M BaCl_2 (pH 6.0) is electrolyzed under following parameters—an anode current density of $15.0 \text{ A}\cdot\text{dm}^{-2}$, a cathode current density of $14.0 \text{ A}\cdot\text{dm}^{-2}$, 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 the results obtained on the laboratory scale, a 50-A cell was designed and operated for the electrolytic preparation of barium chlorate. A stainless steel tank [0.35 m (length) \times 0.25 m (breadth) \times 0.25 m (height)] was fitted with a PVC cover having suitable holes to introduce the anode, cathode, thermometer, and electrolyte and acted as the cell. The anode was again a cylindrical titanium mesh as described in the laboratory scale studies, [0.15 m

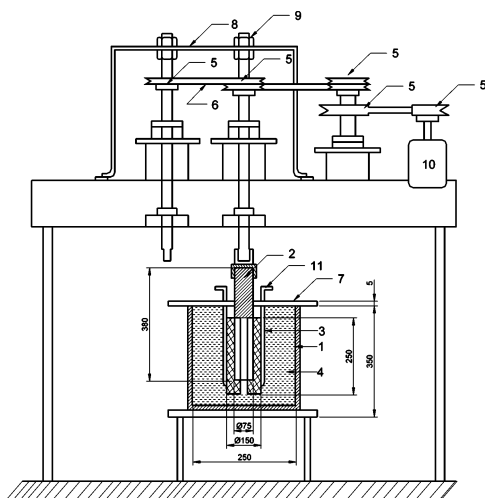


Figure 5. Sketch of a 50-A cell: (1) stainless steel tank, (2) stainless steel cathode, (3) anode, (4) electrolyte, (5) pulleys, (6) V-belts, (7) PVC cover, (8) copper bus bar, (9) mercury cup, (10) 0.5-hp motor, and (11) anode terminal.

Table 4. Results of 50-A Cell for the Production of Barium Chlorate

operating parameters	results
1. electrolyte	BaCl ₂
2. volume of electrolyte	8.5 L
3. initial concentration	
Cl ⁻	1.0 M
ClO ₃ ⁻	0.0 M
4. electrolyte pH	6.0
5. electrolyte temperature	333 K
6. final concentration	
Cl ⁻	0.48 M
ClO ₃ ⁻	0.56 M
7. current passed	50 A
8. anode current density	15.0 A·dm ⁻²
9. cathode current density	14.0 A·dm ⁻²
10. cathode peripheral velocity	1.38 m·s ⁻¹
11. total quantity of current	2733 A·h
12. average voltage	4.0 V
13. current efficiency	56.0%
14. energy consumption	7.6 kW·h·kg ⁻¹

(diameter) × 0.25 m (height)] coated with noble metal oxides (RuO₂/TiO₂/SnO₂ based mixed oxides), while the cathode was a cylindrical stainless steel tube (SS304) [0.075 m (diameter) × 0.38 m (height)] closed at the bottom and fitted to a rotating assembly. The cathode was positioned at the center of the anode assembly at an interelectrode distance of 1 cm. Figure 5 shows a sketch of the cell. 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 M BaCl₂ (pH 6.0), at an anode current density of 15.0 A·dm⁻² and a cathode current density of 14.0 A·dm⁻² with a temperature of 333 K. The cathode peripheral velocity was maintained at 1.38 m·s⁻¹. The current efficiency obtained in the 50-A cell (Table 4) conforms well to the results obtained at laboratory scale.

Conclusion

The electrochemical oxidation of barium chloride to chlorate on noble metal oxide coated electrodes proceeds efficiently, (by achieving a current efficiency of 56% corresponding to the energy consumption of 7.1 kW·h·kg⁻¹ of barium chlorate) when 1.0 M BaCl₂ (pH 6.0) is electrolyzed at an anode current density of 15.0 A·dm⁻², a cathode current density of 14.0 A·dm⁻², a

temperature of 333 K, and with a cathode peripheral velocity of 1.38 m·s⁻¹.

Acknowledgment

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

Literature Cited

- Ibl, N.; Vogt, H. *Comprehensive Treatise of Electrochemistry*; Bockris, J. O'M., Conway, B. E., Yeager, E., Eds.; Plenum Press: New York, 1980; Vol. 2, pp 169–96.
- Foerster, F. *Elektrochemie Wasseriger Losungen*, 3rd ed.; Barth: Leipzig, Germany, 1922; pp 130–142.
- De Valera, V. On the Theory of Electrochemical Chlorate Formation. *Trans. Faraday Soc.* **1953**, *49*, 1338–1351.
- De Valera, V. Anodic oxygen evolution in chlorate cell. *Trans. Faraday Soc.* **1964**, *60*, 1450–1456.
- Ibl, N.; Landolt, D. On the mechanism of anodic chlorate formation in dilute NaCl solution. *J. Electrochem. Soc.* **1968**, *115*, 713–720.
- Landolt, D.; Ibl, N. On the mechanism of anodic chlorate formation in concentrated NaCl solution. *Electrochim. Acta* **1970**, *15*, 1165–1183.
- Jaksic, M. M. Mass transfer and optimization of faradic yields in a chlorate cell process. *Electrochim. Acta* **1976**, *21*, 1127–36.
- Jaksic, M. M. Mutual effect of current density, pH, temperature and hydrodynamic factors on current efficiency in the chlorate cell process. *J. Electrochem. Soc.* **1974**, *121*, 70–79.
- Nechiporenko, N. N.; Voroshilov, P. Kh.; Sivokon, N. V.; Beidin, V. K. Investigation of the anode process in electrolysis of sodium chloride solution. *J. Appl. Chem. USSR* **1960**, *33*, 1798–1807.
- Jaksic, M. M. The effect of pH on graphite wear in a chlorate cell process. *J. Appl. Electrochem.* **1973**, *3*, 219–225.
- Janes, M. Graphite anodes in brine electrolysis. *Trans. Electrochem. Soc.* **1947**, *92*, 23–44.
- Eberil, V. I.; Kupovich, F. V. Influence of the NaCl concentration on magnitude of the anode potential and wear of the graphite anodes in electrochemical preparation of chlorates. *Sov. Electrochem.* **1970**, *6*, 324–326.
- Agapova, R. A.; Elina, L. M. Influence of electrolyte pH on the behavior of graphite anodes under the conditions of electrochemical production of sodium chlorate. *J. Appl. Chem. USSR* **1971**, *44*, 1320–1324.
- Agapova, R. A.; Elina, L. M. Influence of sodium chloride concentration and electrolyte temperature on the stability of graphite anode under the conditions of electrolytic production of chlorate. *J. Appl. Chem. USSR* **1971**, *44*, 1536–1539.
- Eberil, V. I.; Elina, L. M. Some peculiarities of the behavior of graphite anodes in the electrolysis of solutions of NaCl and, in particular, in the production of chlorates. *Sov. Electrochem.* **1970**, *6*, 758–762.
- Shiyapnikov, V. A. Role of the anode material in electrosynthesis of chlorates. *J. Appl. Chem. USSR* **1976**, *49*, 86–89.
- Udupa, H. V. K.; Sampath, S.; Narasimham, K. C.; Sundararajan, S.; Nagalingam, M.; Thiagarajan, N.; Govinda Rao, P.; Raju, C. J.; Chandran, T. J. V.; Kandasamy, S.; Subramanian, G.; Nambodri, P. N. N.; Natarajan, S. Use of graphite substrate lead dioxide anode in the preparation of chlorates. *Ind. J. Technol.* **1966**, *4*, 305–306.
- Udupa, H. V. K.; Sampath, S.; Narasimham, K. C.; Nagalingam, M.; Thiagarajan, N.; Subramanian, G.; Natarajan, S.; Subbiah, P.; Palanisamy, R.; John Peter, S.; Pushpavanam, S.; Sadagopalan, M. Production of sodium chlorate using graphite substrate lead dioxide anodes: scaling up to 800 amp cells. *Ind. J. Technol.* **1971**, *9*, 257–261.
- Ilin, K. G.; Skripchenko, V. I. Effect of the nature of the electrolyte cation on the anode process in the electrolysis of solutions of alkali and alkaline earth metal chlorides. *Sov. Electrochem.* **1961**, *3*, 261–266.
- Pushpavanam, S.; Mohan, S.; Vasudevan, S.; Ravichandran, S.; Narasimham, K. C. Magnesium chlorate by electrolysis of magnesium chloride. *Bull. Electrochem.* **1990**, *6*, 422–423.
- Vasudevan, S.; Pushpavanam, S.; Mohan, S.; Narasimham, K. C. Electrolytic preparation of strontium chlorate from strontium chloride. *Proceedings of the Second National Conference on Electrochemicals*, held at IIT, Bombay, India, 1990.
- Vasudevan, S.; Mohan, S.; Pushpavanam, S.; Narasimham, K. C. Electrolytic preparation of magnesium perchlorate. *J. Appl. Electrochem.* **1992**, *22*, 877–882.

- (23) Vasudevan, S.; Pushpavanam, S.; Mohan, S.; Narasimham, K. C. Electrolytic Preparation of magnesium chlorate from magnesium chloride. *J. Appl. Electrochem.* **1992**, *22*, 1201–1204.
- (24) Pushpavanam, S.; Narasimham, K. C.; Vasu, K. I. Structural properties of Ru-Ti-Sn mixed oxide coatings. *Bull. Electrochem.* **1988**, *4*, 979.
- (25) Vogel, A. I. *Quantitative Inorganic Analysis*; Libgnabs Green: London, 1964; pp 259–260.
- (26) Grant, J. *Clowes and Coleman's Quantitative Analysis*; Churchill: London, 1974; pp 176–178.
- (27) West, T. S.; Sykes, A. S. *Analytical Applications of Diamino Ethane Tetra Acetic Acid*; The British Drug House Ltd: England, 1960; p 59.
- (28) Vanmuylder, J.; Pourbaix, M. In *Atlas of Electrochemical Equilibria in Aquous Solutions: Barium*; Vanmuylder, J., Pourbaix, M., Eds.; Pergamon: New York, 1966; pp 139–153.
- (29) Kuhn, A. T.; Chan, C. Y. pH changes at near electrode surfaces. *J. Appl. Electrochem.* **1983**, *13*, 189–207.
- (30) Kudrayavstev, N. T.; Yarlykov, M. M.; Melnikova, M. M. Investigation of the pH of the catholyte layer in electrolytes during electrodeposition of nickel and iron. *J. Appl. Chem. USSR* **1965**, *38*, 554–561.
- (31) Vasudevan, S.; Mohan, S.; Pushpavanam, S.; Narasimham, K. C. Chlorates and perchlorates of strontium by electrolysis. *Bull. Electrochem.* **1993**, *9*, 693–695.
- (32) Vogt, H. Chlorate electrosynthesis current efficiency equations based on dimensionless groups. *J. Appl. Electrochem.* **1992**, *22*, 1185–1191.
- (33) Linke, W. F. *Solubilities*; American Chemical Society: Washington, D.C. 1964; Vol. 2, p 516.
- (34) Deligianni, H.; Romankiw, L. T. A rotating pH electrode for measurement of surface pH during electrolysis; study of NiFe electrodeposition. Extended Abstracts, *The Electrochemical Society, Fall Meeting*, Seattle, WA, **1990**, 90–2, 498.

Received for review September 11, 2005

Revised manuscript received February 22, 2006

Accepted February 28, 2006

IE051018R