

Optimization of the process parameters for an electrochemical preparation of strontium perchlorate

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Abstract—The electrochemical preparation of strontium perchlorate, Sr(ClO₄)₂, from strontium chlorate employing platinum anode and a rotating stainless steel cathode is described. The effect of electrolyte concentration, current density, pH and temperature of the electrolyte and cathode rotation on current efficiency for the preparation of strontium perchlorate was studied. A maximum current efficiency of 42% was achieved corresponding to an energy consumption of 6.1 kWh. kg⁻¹.

Key words: Electrochemical, Oxidation, Strontium Perchlorate, Rotating Cathode

INTRODUCTION

The preparation of alkali metal perchlorates by electrolysis of the corresponding chlorates has been studied by various authors [1]. Schumacher [2] reported other methods for manufacturing of perchlorates from different raw materials. The mechanism, kinetic aspects and electrode materials for perchlorate formation were dealt with within the literature [3-7]. After understanding the mechanism of perchlorate formation, attempts were made to study the different anode materials like platinum [8], and lead dioxide anode [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 take place in a cell when it is used as an anode, still platinum is the material of choice for commercial cells. So in the present case, platinum is used as anode material. However, Platinum-clad tantalum, platinum-coated tantalum and platinum-coated titanium are the future anode materials would decrease the amount of platinum and thereby the cost of production of strontium perchlorate.

Literature contains limited publication dealing with investigations on production of alkaline earth metal perchlorates by electrolysis of chlorate, and the only publication that relates to the preparation of alkaline earth metal chlorates by electrolysis 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 corresponding metal hydroxides, which are having poor solubility as against the hydroxides of alkali metals. The authors were successful in preparing magnesium and barium chlorate [10-13] where metal oxide coated titanium as anode and a rotating cathode was employed to minimize the precipitation of corresponding metal hydroxides.

Therefore, the main objective of this study is to prepare strontium perchlorate from strontium chlorate, by electrochemical method, using platinum and rotating stainless steel as anode and cathode, respectively. To optimize the parametric conditions, the various parameters like effect of electrolyte concentration, pH and temperature, current density and cathode rotation on current efficiency was investigated. Strontium perchlorate is used as secondary injection thrust vector control (SITVC) of the first stage satellite launch vehicles.

1. Perchlorate Formation Reactions and Mechanisms

Chlorate is oxidized to perchlorate according to the overall reaction:



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 [14].



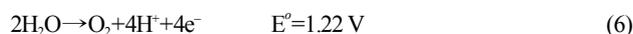
According to the second mechanism, the primary step is the direct discharge of chlorate ion at the anode with the formation of free chlorate radical, which then reacts with water to form perchlorate [5,6].



However, under alkaline conditions, the formation of perchlorate, may takes place as follows [15]:



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



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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 solubility as indicated below, will also be encountered in the case of alkaline earth metal perchlorates.



Where, $M = Sr^{2+}$

According to Sr^{2+} - H_2O Pourbaix diagram [16], strontium hydroxide formation is predicted by the following reaction:



During the electrolysis, according to reaction 8, strontium hydroxide forms an adherent coating over the cathode, in the pH of 14.0, and can protect the metal surface and hinder further cathodic reaction. The precipitation of this metal hydroxide depends on factors such as electrolyte concentration, pH, temperature, current density and cathode rotation.

MATERIALS AND METHODS

1. 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, pH sensor, 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 inter-electrode distance of 1.0 cm. The platinum foil of size 0.025 m (width) × 0.085 m (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 strontium chlorate solution obtained from the electrolysis of strontium chloride was used as electrolyte.

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 of solution was used for each experiment, which was used as the electrolyte. The electrolyte pH was monitored with 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 repeated three times for reproducibility. The effect of various parameters on current efficiency was determined.

2. Analysis

Chloride: Chloride was estimated by using 0.1 N silver nitrate (Ranbaxy, India) and 1% K_2CrO_4 (Ranbaxy, India) [17].

Chlorate: Chlorate was estimated iodometrically by using 0.1 N thiosulfate in presence of KBr (3.0 g), conc. HCl (30 ml) and 10% KI (10 ml) [18].

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

Strontium: Strontium was determined by titration with 0.1 N EDTA (Analar Grade, BDH, India) at pH 10 using Solochrome Black-T (BDH, India) as an indicator [19].

RESULTS AND DISCUSSION

1. Effect of Electrolyte Concentration

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 complementary current efficiencies. Furthermore, the influence of pH on the equilibrium potentials for both reactions 1 and 6 is the same [14] 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, because of their progressive adsorption at the interface as electrostatic attraction increases with potential. Consequently, the water molecules adsorbed at the interface are gradually displaced by ClO_3^- ions, which thus hinders the primary discharge of water and consequently oxygen evolution. This is evidenced, in particular, by the strong inflection generally 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. 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 increasing the current efficiency.

The opposing trend with strontium chlorate electrolysis must be connected with the removal of strontium as its hydroxide with the corresponding anodic evolution of oxygen. It is found [20] that the $pH_{(s)}$ increases with increasing the 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 $pH_{(s)}$ can easily become alkaline, resulting in the precipitation of $Sr(OH)_2$ and deposit on the cathode surface. The loss of Sr^{2+} (in electrolyte) as $Sr(OH)_2$ increases 0.04 to 0.06 M when the concentration of strontium chlorate increases from 1.5 M to 2.5 M, and consequently the current efficiency decreases from 42 to 34%. Fig. 1 shows the variation of current efficiency and energy consumption with concentration for the formation of strontium perchlorate.

2. Effect of pH

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

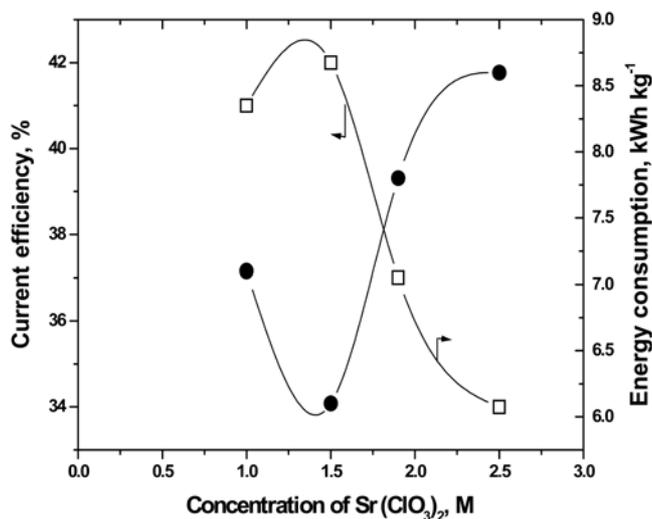


Fig. 1. Variation of current efficiency and energy consumption with concentration. Conditions, electrolyte pH: 6.0; electrolyte temperature: 333 ± 2 K; current density: 30.0 A dm^{-2} ; cathode peripheral velocity: 1.38 m s^{-1} .

fact which is explained [3] due to the discharge potential for oxygen at platinum being lower in alkaline than in acid solutions. Furthermore, 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, or 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 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 [14]. It is also reported [14] that if the solution is made alkaline at the anode the efficiency of perchlorate production falls off rapidly, a fact that 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 consequently drops 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 [14]. During this time oxygen is evolved and efficiency necessarily falls. Fig. 2 shows the variation of current efficiency with energy consumption for different pHs of the electrolyte for the preparation of strontium perchlorate. At pH 4.0 the current efficiency is less than that of 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 pH of the layer adjacent to the cathode be-

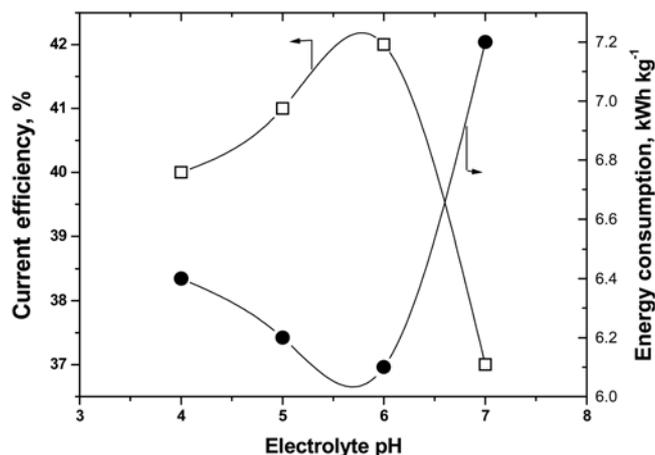


Fig. 2. Variation of current efficiency and energy consumption with electrolyte pH. Conditions, electrolyte concentration: 1.5 M ; electrolyte temperature: $333 \pm 2 \text{ K}$; current density: 30.0 A dm^{-2} ; cathode peripheral velocity: 1.38 m s^{-1} ; theoretical quantity of charge passed: 64.0 Ah .

comes more alkaline, thereby favoring the precipitation of metal (Sr^{2+}) hydroxide and also resulting in the ease of oxygen discharge from a solution containing high concentration of OH^- ions, and consequently reduction in current efficiency for the preparation of perchlorate.

3. Effect of Temperature

Earlier workers ascribed the effect of temperature on perchlorate formation to various factors. It is reported that [21] 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^- ion caused by the increased dissociation of water at higher temperatures.

Bennett and Meck [14] state that an increase in electrolyte temperature decreases the current efficiency markedly because of the concentration of active oxygen present at the anode at any given time. Increased temperature favors the formation of molecular oxygen (reaction 6 - loss reaction) resulting a lower active oxygen concentration, and consequently a lower oxidation power resulting decrease in current efficiency. A sufficient higher current density at high temperature would, however, tend to increase the rate of production of active oxygen (reaction 2 - required reaction) and increase its concentration, resulting increase in current efficiency. With the increase of current density it can, therefore, be expected to obtain a rise in efficiency of chlorate oxidation, 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 to have better current efficiency with increasing temperature, which has been realized experimentally. At the anode current density of $24 \text{ A} \cdot \text{dm}^{-2}$ the current efficiency was found to be 39% for strontium perchlorate formation by maintaining the temperature of 333 K. This was raised to 45% at $37 \text{ A} \cdot \text{dm}^{-2}$, the temperature remaining constant at 333 K. Fig. 3 shows the effect of temperature of the electrolyte on current efficiency for the preparation of strontium perchlorate. In the present case the rise in temperature increases the current efficiency up to the temperature studies. This higher current efficiency with increase of temperature can also be attributed to higher solubility of strontium hydroxide at

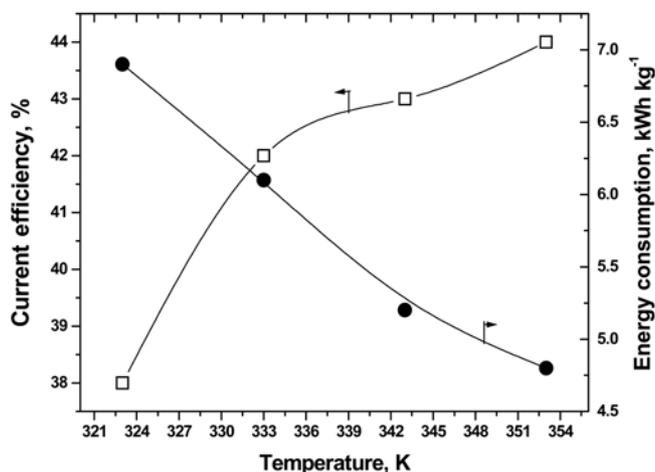


Fig. 3. Variation of current efficiency and energy consumption with cathode current density. Conditions, electrolyte concentration: 1.5 M; electrolyte pH: 6.0; electrolyte temperature: 333 \pm 2 K; anode current density: 30.0 A dm²; cathode peripheral velocity: 1.38 m s⁻¹; theoretical quantity of charge passed: 64.0 Ah.

higher temperatures [22], in addition to what has been discussed above.

4. Effect of Cathode Current Density

It is found that [23,24], $pH_{(s)}$ is increased by increasing the cathode current density and favoring the hydroxide formation. The results in the present instance confirm the same. In the present study, it is visually found that the loss of Sr²⁺ as strontium hydroxide increases with increasing cathode current density, thereby resulting in the lowering of current efficiency. Fig. 4 shows the effect of cathode current density on current efficiency for the preparation of strontium perchlorate.

5. Effect of Cathode Peripheral Velocity

Even in the absence of mechanical agitation, the cathode surface

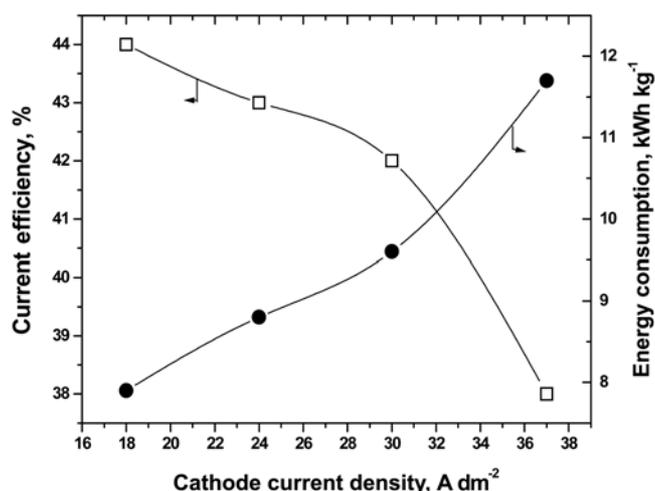


Fig. 4. Variation of current efficiency and energy consumption with electrolyte temperature. Conditions, electrolyte concentration: 1.5 M; electrolyte pH: 6.0; current density: 30.0 A dm²; cathode peripheral velocity: 1.38 m s⁻¹; theoretical quantity of charge passed: 64.0 Ah.

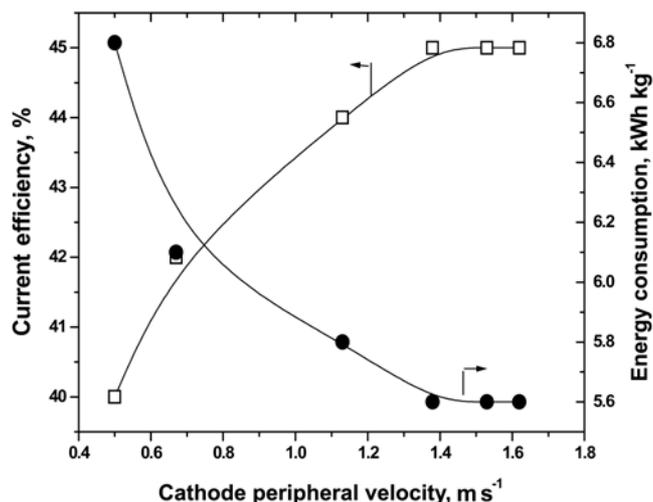


Fig. 5. Variation of current efficiency and energy consumption with cathode peripheral velocity. Conditions, electrolyte concentration: 1.5 M; electrolyte pH: 6.0; electrolyte temperature: 333 \pm 2 K; current density: 30.0 A dm²; theoretical quantity of charge passed: 64.0 Ah.

layer is continuously disturbed due to hydrogen evolution, so that the $pH_{(s)}$ will change only gradually. In the present case the gas evolution is insufficient to maintain the $pH_{(s)}$ 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 $pH_{(s)}$ as against that with slower rotation. Fig. 5 shows that the current efficiency increases with cathode rotation and it is maximum at a peripheral velocity of 1.38 m s⁻¹. This is due to the effective removal of OH⁻ ions at the cathode by consequently minimizing the precipitation of strontium hydroxide.

From the above results it is found that the maximum current efficiency of 42% with an energy consumption of 6.1 kWh kg⁻¹ was achieved when 1.5 M Sr(ClO₃)₂ (pH 6.0) was electrolyzed under the following parameters: current density of 30.0 A dm⁻², a temperature of 333 K and with a cathode peripheral velocity of 1.38 m s⁻¹.

6. 50-A Bench Scale Experiments

On the basis of results obtained on the laboratory scale, a 50A cell was designed, fabricated and operated for the electrolytic preparation of strontium perchlorate. A stainless steel tank [0.35 (length) \times 0.25 (width) \times 0.25 m (height)] was fitted with PVC cover having suitable holes to introduce anode, cathode, thermometer and the electrolyte acted as the cell. A platinum anode [0.17 (width) \times 0.18 m (height)] was used. Two cylindrical stainless steel tubes [0.075 (diameter) \times 0.21 m (height)] closed at the bottom and fitted to the rotating assemblies acted as cathode and were positioned on either side of the anode with an inter-electrode distance of 1 cm. Fig. 6 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 1.5 M Sr(ClO₃)₂ (pH 6.0), at a current density of 30.0 A dm⁻² with a temperature of 333 K. The cathode peripheral velocity was main-

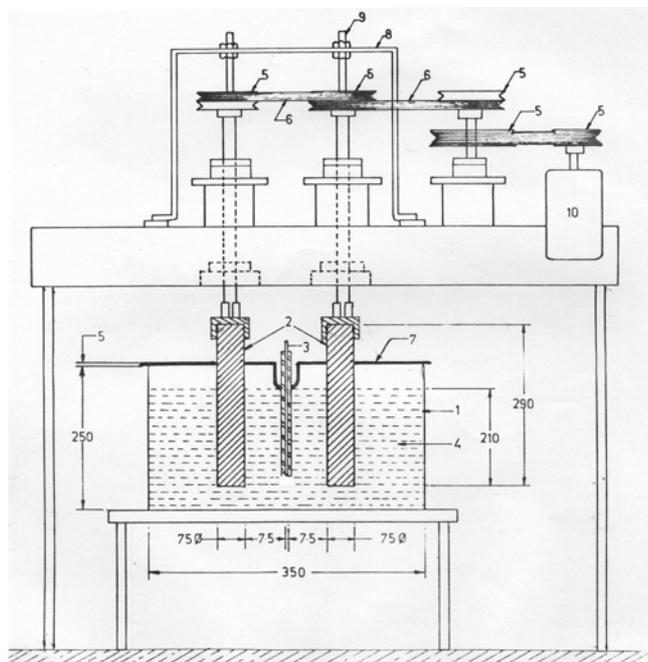


Fig. 6. A sketch of 50 A cells.

- | | |
|----------------------------|-------------------|
| 1. Stainless steel tank | 6. V-belts |
| 2. Stainless steel cathode | 7. PVC cover |
| 3. Anode | 8. Copper bus bar |
| 4. Electrolyte | 9. Mercury cup |
| 5. Pulleys | 10. 0.5-hp motor |

Table 1. Results of 50 A cell for the production of strontium perchlorate

Operating parameters	Results
1. Electrolyte	: $\text{Sr}(\text{ClO}_3)_2$
2. Volume of electrolyte	: 8.5-L
3. Initial concentration	
ClO_3^-	: 1.5 M
ClO_4^-	: 0.0 M
4. Electrolyte pH	: 6.0
5. Electrolyte temperature	: 333 K
6. Final concentration	
ClO_3^-	: 0.40 M
ClO_4^-	: 0.54 M
7. Current passed	: 50 A
8. Anode current density	: 30.0 A dm^{-2}
9. Cathode current density	: 30.0 A dm^{-2}
10. Cathode peripheral velocity	: 1.38 m S^{-1}
11. Average voltage	: 6.9 V
12. Current efficiency	: 42.0%
13. Energy consumption	: 6.1 kWh kg^{-1}

tained at 1.38 m s^{-1} . The current efficiency obtained in the 50 A cell (Table 1) conforms well to the results obtained at laboratory scale.

CONCLUSIONS

The electrochemical oxidation of strontium chlorate to perchlor-

ate can proceed efficiently when $1.5 \text{ M Sr}(\text{ClO}_3)_2$ (pH 6.0) is electrolyzed using platinum anode and stainless steel cathode with a current density of 30 A dm^{-2} , temperature of 333 K and anode peripheral velocity of 1.38 m s^{-1} to achieve current efficiency of 42% corresponding to an energy consumption of 6.1 kW h kg^{-1} .

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