SHORT COMMUNICATION

Electrolytic preparation of magnesium chlorate from magnesium chloride

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1. Introduction

The preparation of alkali metal chlorates by electrolysis of the corresponding chlorides has been studied by various authors [1]. However, reports of electrochemical methods for preparing alkaline earth metal chlorates are scarce, even though their salts have some specialty applications [2, 3]. In the case of the electrolysis of magnesium chloride, the precipitation of the magnesium hydroxide due to its low solubility is problematic, leading to a loss in current efficiency. Further, heavy deposits of magnesium hydroxide form on the cathode with consequently increased cell voltage. This difficulty has been obviated using a rotating stainless steel cathode which minimises hydroxide precipitation. A titanium coated metal oxide anode was used for the oxidation of magnesium chloride to magnesium chlorate. This paper presents results for the preparation of magnesium chlorate from magnesium chloride [4].

2. Experimental details

The electrochemical cell consisted of a 500 cm³ glass vessel fitted with a PVC cover having suitable holes to introduce the electrodes, a pH sensor and a thermometer. The cathodes were cylindrical stainless steel rods of different dimensions (80 mm (h) × 10 mm (dia.), 70.5 mm (h) × 15 mm (dia.) and 90 mm (h) × 25 mm (dia.)). Depending on the parameters, each cathode was fitted to a rotating assembly and positioned at the centre of the cell. Noble metal oxide coated titanium mesh or strip(s) [5] surrounding the cathode acted as anode with an inter-electrode distance of 5 mm. The temperature of the electrolyte was controlled to the desired value with a variation of ± 1 K, by adjusting the rate of flow of thermostatically controlled water through an external glass cooling spiral. 450 cm³ of electrolyte, prepared from laboratory grade magnesium chloride, was used for each experiment.

Electrical connection to the cathode was via a mercury cup. The electrolyte pH was regulated to ± 0.05 pH units by adding either acid or base. Each experiment was continued until the theoretical charge had been passed. Chloride was estimated using Mohr's method [6]; chlorate was estimated iodometrically [7] and magnesium was determined by titration with EDTA at pH 10 using Solochrome Black T as indicator [8].

3. Results and discussion

The reactions occurring in a chlorate cell have been studied in detail in the case of alkali metal chlorates [1]. The primary electrochemical reactions are chlorine evolution at the anode and OH^- formation at the cathode, which, depending on the pH, subsequently undergo chemical or electrochemical reactions to give chlorate. However, there are a number of secondary or side reactions leading to a decrease in the current efficiency [9]. In the case of alkaline earth metal cations an additional cathode loss reaction viz., precipitation of metal hydroxide,

$$M^{2+} + 2OH^- \rightarrow M(OH)_2\downarrow \qquad (1)$$

is encountered due to the low solubility. The precipitation of these metal hydroxides depends on factors such as cation concentration, pH, current density, temperature and cathode rotation.

3.1. Effect of initial magnesium chloride concentration

The results for different initial concentrations of magnesium chloride ranging from 1.0 to 3.0 M and maintaining other parameters constant, are given in Fig. 1. The current efficiency increased with increasing initial concentration and was maximum at 2.0 to 2.5 M; beyond this it decreased. This is because at higher
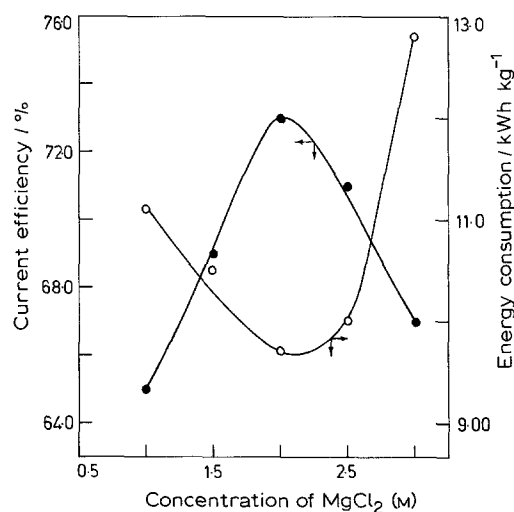
Fig. 1. Variation of current efficiency and energy consumption with concentration of magnesium chloride. Conditions: Electrolyte: pH 6.0; temperature: 333 K; anode current density: 15.0 A dm⁻²; cathode current density: 14.0 A dm⁻² and cathode peripheral velocity: 40 m min⁻¹.
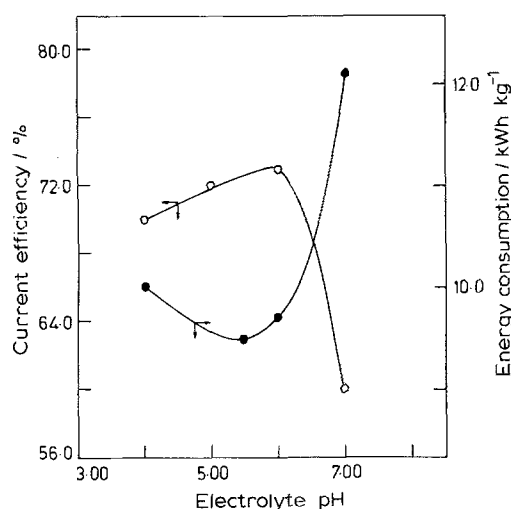
Fig. 2. Variation of current efficiency and energy consumption with electrolyte pH. Conditions: Electrolyte concentration: $185\,g\,dm^{-3}$; temperature: 333 K; anode current density: $15.0\,A\,dm^{-2}$; cathode current density: $14.0\,A\,dm^{-2}$ and cathode peripheral velocity: $40\,m\,min^{-1}$.
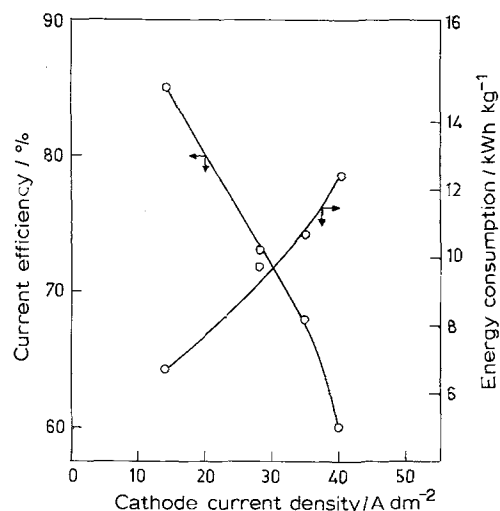
Fig. 3. Variation of current efficiency and energy consumption with cathode current density. Conditions: Electrolyte concentration: $185\,g\,dm^{-3}$; electrolyte: pH 6.0; temperature: 333 K; anode current density: $15.0\,A\,dm^{-2}$; cathode peripheral velocity: $40\,m\,min^{-1}$.

concentrations the precipitation of magnesium hydroxide is increased, thereby reducing the current efficiency.

### 3.2. Effect of pH and cathode current density

Figures 2 and 3 show the effect of electrolyte pH (ranging from 4.0 to 7.0) and cathode current density, respectively, on current efficiency. Unlike the alkali metal chloride reactions, the pH and cathode current density play a significant role in determining 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 [10]. The change in $pH_{(s)}$ (ΔpH) is related to the bulk pH $[pH_{(b)}]$ and current density. At lower current densities ΔpH is not appreciable whereas at higher current densities ΔpH increases significantly, even when $pH_{(b)}$ is lower [10]. In this case current efficiency is found to be maximum around pH 6.0. But when $pH_{(b)}$ becomes 7.0, $pH_{(s)}$ is more

alkaline, thereby favouring the precipitation of magnesium hydroxide and releasing an equivalent amount of free chlorine with a loss of efficiency [11]. Below $pH_{(b)}$ 5.00, it is well known that the efficiency decreases due to evolution of free chlorine [1]. Figure 2 shows this trend; the current efficiency was maximum around pH 5.5 to 6.0.

Kurdrayavstev et al. [12], found that in the case of KCl solution, using a platinum electrode, the surface pH increased with increasing current density. Starting with an initial pH of 4.8 the pH becomes 5.9 and 14.0 at current densities of 0.1 and 100 A m^{-2}, respectively. At still higher current densities the increase in $pH_{(s)}$ is higher. In the present instance, with high current density the $pH_{(s)}$ can easily reach ≥ 14, thereby becoming alkaline, resulting in the precipitation of metal hydroxide on the cathode surface.

According to the Mg-H$_2$O Pourbaix diagram [13], magnesium hydroxide formation is predicted by

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \qquad (2)$$
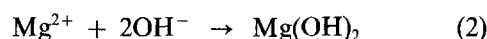
$$\log[Mg^{2+}] = \log K - 2pH \qquad (3)$$

Table 1. Effect of anode current density on current efficiency for the preparation of magnesium chlorate

S. No.	Anode current density/$A\,dm^{-2}$	Voltage/V	Final concentration /$g\,dm^{-3}$		Loss of Mg^{2+}/$g\,dm^{-3}$	Current efficiency for $Mg(ClO_3)_2$ formation/%	Energy consumption for $Mg(ClO_3)_2$/ $kWh\,kg^{-1}$
			Cl^-	ClO_3^-			
1	5.00	3.9	15.0	242.0	10.2	64	10.2
2	10.00	4.0	11.0	260.0	8.7	69	9.8
3	15.00	4.2	9.7	275.0	7.9	73	9.7
4	20.00	4.3	7.1	301.0	6.8	78	9.3

Concentration of $MgCl_2$: $185.0\,g\,dm^{-3}$; electrolyte pH 6.00.
Temperature: $333 \pm 1\,K$; cathode current density: $40\,A\,dm^{-2}$.
Cathode peripheral velocity: $40\,m\,min^{-1}$.
Theoretical quantity of electricity passed: 273 A h.

Table 2. Effect of temperature on current efficiency for the preparation of magnesium chlorate

S. No.	Temperature/K	Voltage/V	Final concentration /g dm^{-3}		Loss of Mg^{2+}/g dm^{-3}	Current efficiency for Mg(ClO$_3$)$_2$ formation/%	Energy consumption for Mg(ClO$_3$)$_2$/ kWh kg^{-1}
			Cl$^-$	ClO$_3^-$			
1	313	4.3	4.0	210.0	8.9	55	13.0
2	323	4.2	7.3	242.0	8.1	64	11.0
3	333	4.2	9.7	275.0	7.9	73	9.7
4	343	3.9	8.0	298.0	7.1	79	8.3

Concentration of MgCl$_2$: 185.0 g dm^{-3}; electrolyte pH 6.00.
Anode current density: 15.0 A dm^{-2}, cathode current density: 40 A dm^{-2}.
Cathode peripheral velocity: 40 m min^{-1}.
Theoretical quantity of electricity passed: 273 A h.

The magnesium hydroxide forms an adherent coating over the cathode in the pH range 8.5 to 11.5. The value of pH$_{(s)}$ goes beyond 11.5 as current density increases and, consequently, the precipitation of magnesium hydroxide occurs with a reduction in the overall current efficiency. Figure 3 shows this trend; the current efficiency decreases with increasing cathode current density from 14.0 to 40.0 A dm^{-2}.

3.3. Effect of anode current density

The results of the influence of anode current density on current efficiency are shown in Table 1, which indicate that the current efficiency increases with increasing anode current density. It has been reported [1] that increasing the anode current density results in an increase in current efficiency, which is in agreement with the results obtained in the present experiments. However, as the cell voltage increases with increasing current density, consequently resulting in higher energy consumption, a compromise has to be arrived in selecting the current density for further investigation. It was thus maintained at 15.0 A dm^{-2} for subsequent experiments.
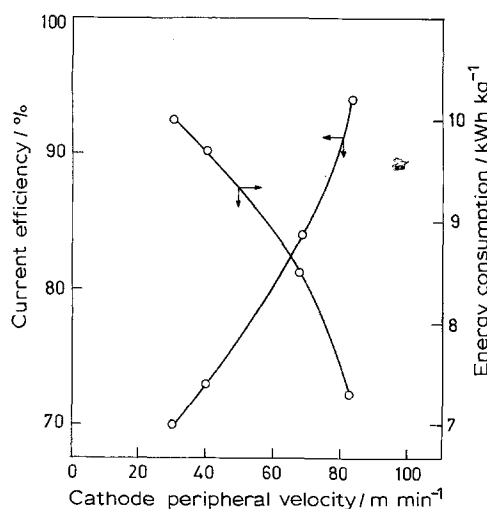

Fig. 4. Variation of current efficiency and energy consumption with cathode peripheral velocity. Conditions: Electrolyte concentration: 185 g dm^{-3}; electrolyte: pH 6.0; temperature: 333 K; anode current density: 15.0 A dm^{-2} and cathode current density: 14 A dm^{-2}.

3.4. Effect of temperature

Due to the higher solubility of magnesium hydroxide [14] as well as the increase in the rate of chlorate formation at higher temperature [1], the current efficiency is expected to increase with increasing temperature. This has been confirmed by the results in Table 2, where an increase of current efficiency from 55 to 79% is observed on increasing the temperature from 313 to 343 K.

3.5. 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 pH$_{(s)}$ may change only gradually. In the present case the gas evolution is probably insufficient to maintain the pH$_{(s)}$ at the desired value. To achieve such pH control the cathode was rotated. It has been found [15] that increasing the peripheral velocity produces the desired value of pH$_{(s)}$ as against that with slower rotation. Figure 4 shows that current efficiency increases with cathode peripheral velocity and is maximum at 82 m min^{-1}. This is due to the effective removal of OH$^-$ ions produced at the cathode, consequently minimizing the precipitation of magnesium hydroxide.

In general the current efficiencies during the electrolysis of alkaline earth metal chlorides are less than those for chlorides of sodium or potassium [2]. This may be attributed due to the differences in the solubility of the respective hydroxides.

4. Conclusion

The electrochemical oxidation of magnesium chloride to chlorate proceeds efficiently, when 2 M MgCl$_2$ (pH 6.00) is electrolysed 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 about 60–80 m min^{-1}, to achieve current efficiencies of 80–90%, corresponding to the energy consumptions of 8.5 to 7.3 kWh kg^{-1} of magnesium chlorate.

Acknowledgement

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