

Electrolytic preparation of magnesium perchlorate

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The electrochemical preparation of magnesium perchlorate from magnesium 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 magnesium perchlorate was studied. A maximum current efficiency of 65–72% was achieved. Based on the results obtained on the laboratory scale, a 100 A cell was designed, fabricated and operated.

1. Introduction

Among the various known methods, the electrolytic route is economical for the manufacture of a number of inorganic chemicals and especially perchlorates [1]. A variety of perchlorates, such as ammonium, sodium, potassium etc., are well known and their applications have been reported previously [2]. But work on electrochemical methods of preparing alkaline earth metal perchlorates are scanty. Because, in the case of alkaline earth metal salts, the precipitation of the corresponding metal hydroxides causes great problems, leading to a loss in current efficiency. Further, heavy deposits of magnesium hydroxide on the cathode prevents continuous electrolysis. This difficulty has been obviated by using the rotating cathode technique in this work and this paper presents results for the preparation of magnesium perchlorate using a platinum anode and a rotating stainless steel cathode.

Anhydrous magnesium perchlorate (anhydron) is a well known powerful desiccant. Another potential application of magnesium perchlorate is its use as electrolyte in high energy density batteries [3–5] and Mg/MnO₂ batteries [6].

2. Experimental details

The electrolytic cell consisted of a 500 cm³ Pyrex tall form beaker fitted with a PVC cell cover with slots to introduce the electrolyte, pH sensor, thermometer and electrodes. The anode was either platinum foil or platinum coated titanium [7] of size 25 mm (*b*) × 85 mm (*h*). Cylindrical stainless steel rods of 90 mm height with diameters of 10, 15 and 25 mm were employed as cathodes. The cathode was fitted to a rotating assembly and positioned at the centre of the cell at an interelectrode distance of 5 mm. The cell assembly was placed in an outer vessel containing glass spiral surrounding the cell assembly and immersed in water. This entire assembly was kept in a thermocole box. The temperature of the water and consequently the temperature of electrolyte in the cell was controlled to the desired value with a variation of ± 1°C, by adjusting the rate of flow of thermostatically controlled water through the glass spiral.

The magnesium chlorate solution obtained from the electrolysis of magnesium 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 h.p. motor. A d.c. current was supplied from a rectifier (25 A, 0–12 V). 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.

The constituents of electrolyte, viz., Cl⁻, ClO₃⁻, ClO₄⁻ and Mg(II) were analysed periodically [8].

The cumulative current efficiency was calculated for each experiment. The effect of various parameters on current efficiency was determined.

3. Results

3.1. Effect of initial concentration of magnesium chlorate on current efficiency

The results of the experiments carried out with different initial concentrations of magnesium chlorate ranging from 1.0 to 3.0 M (and maintaining other parameters constant), are given in Fig. 1. The current efficiency for perchlorate formation increases significantly up to an initial concentration of magnesium chlorate of 2 M and above this value it decreases rapidly.

3.2. Effect of pH on current efficiency

Table 1 shows the effect of electrolyte pH on the current efficiency for the formation of magnesium perchlorate. The current efficiency was found to be maximum around pH 6.0. It is also well known that lower pH (< 5.0) can lead to the evolution of chlorine gas when pH is adjusted with dilute HCl. However at higher pH (> 7.0) the precipitation of magnesium hydroxide is more pronounced under these conditions.

3.3. Effect of anode and cathode current densities on current efficiency

The current efficiency was found to increase with

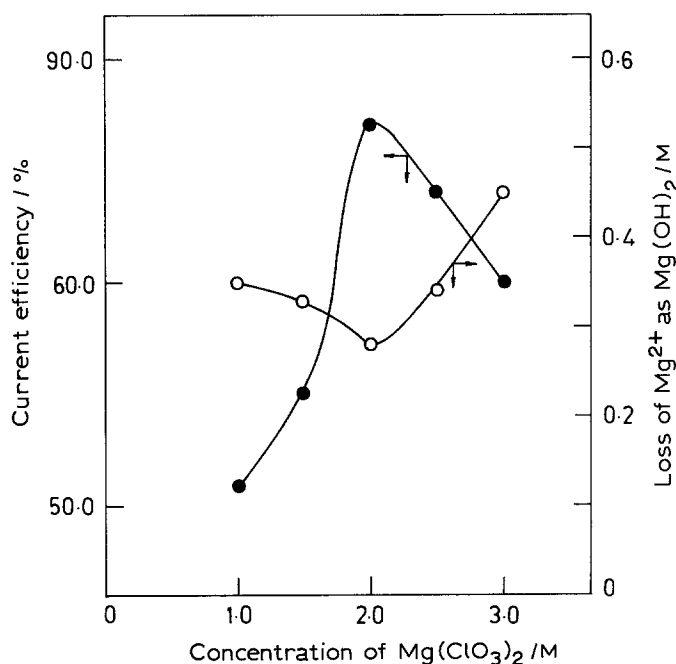


Fig. 1. Variation of current efficiency and loss of Mg^{2+} by precipitation as $Mg(OH)_2$ with concentration of magnesium chlorate. Conditions: electrolyte pH 6.00; temperature 333 ± 1 K, anode current density 30 A dm^{-2} , cathode current density 32 A dm^{-2} , cathode rotation (peripheral velocity) 40 m min^{-1} and theoretical quantity of electricity passed 100 Ah.

increasing anode current density as seen in Table 2. The cell voltage also increases with increase of current density. However, it was maintained at 30 A dm^{-2} for subsequent experiments. Increase in the cathode current density decreases the current efficiency (Table 3). The pH of the cathode surface becomes more alkaline with increase in current density, thereby favouring the precipitation of magnesium hydroxide and, consequently, reduction in the current efficiency.

3.4. Effect of temperature on current efficiency

Figure 2 shows the effect of electrolyte temperature on the current efficiency for the temperature range 323–353 K. The current efficiency increases from 60–69% with increasing temperature. This may be due to the increasing solubility of magnesium hydroxide [9].

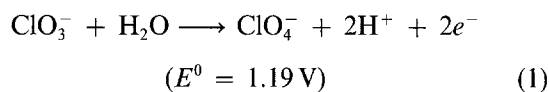
3.5. Effect of cathode rotation on current efficiency

Since the rotation of the cathode has a beneficial effect by decreasing the precipitation of alkaline earth metal hydroxides (in this case $Mg(OH)_2$), the effect of cathode rotation or peripheral velocity on current

efficiency has been studied (even though the process is anodic) and the results are shown in Fig. 3. The results show that the current efficiency increases with increasing cathode peripheral velocity and a maximum current efficiency of 72% is achieved at 82 m min^{-1} , indicating that the higher speed of rotation minimizes the precipitation of magnesium hydroxide.

4. Discussion

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



Although several mechanisms have been proposed [10], 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 [11].

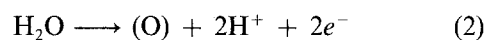


Table 1. Effect of pH on current efficiency for the preparation of magnesium perchlorate

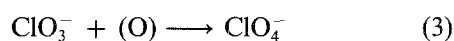
| S. No. | Initial pH | Voltage/V | Final concentration / g dm^{-3} | | Loss of Mg^{2+}/M | Current efficiency for $Mg(\text{ClO}_4)_2$ formation/% | Energy consumption for $Mg(\text{ClO}_4)_2/\text{kWh kg}^{-1}$ |
|--------|------------|-----------|--|------------------|---------------------|---|--|
| | | | ClO_3^- | ClO_4^- | | | |
| 1 | 4.00 | 6.5 | 27.0 | 315.0 | 0.41 | 60 | 5.20 |
| 2 | 5.00 | 6.4 | 30.0 | 325.0 | 0.32 | 63 | 4.90 |
| 3 | 6.00 | 6.9 | 15.0 | 350.0 | 0.28 | 67 | 4.90 |
| 4 | 7.00 | 6.9 | 25.0 | 318.0 | 0.35 | 61 | 5.40 |

Concentration of $Mg(\text{ClO}_3)_2$: 352.0 g dm^{-3} , temperature: 333 ± 1 K
 Anode current density: 30 A dm^{-2} , cathode current density: 32 A dm^{-2}
 Cathode peripheral velocity: 40 m min^{-1}
 Theoretical quantity of electricity passed: 100 Ah

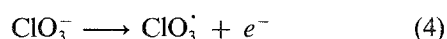
Table 2. Effect of anode current density on current efficiency for the preparation of magnesium perchlorate

| S. No. | Anode current density/A dm ⁻² | Voltage/V | Final concentration /g dm ⁻³ | | Loss of Mg ²⁺ /M | Current efficiency for Mg(ClO ₄) ₂ formation/% | Energy consumption for Mg(ClO ₄) ₂ /kWh kg ⁻¹ |
|--------|--|-----------|---|-------------------------------|-----------------------------|---|---|
| | | | ClO ₃ ⁻ | ClO ₄ ⁻ | | | |
| 1 | 24.00 | 6.2 | 30.0 | 325.0 | 0.32 | 63 | 4.80 |
| 2 | 30.00 | 6.9 | 15.0 | 350.0 | 0.28 | 67 | 4.90 |
| 3 | 37.00 | 7.0 | 10.0 | 362.0 | 0.23 | 69 | 4.90 |

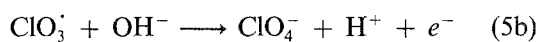
Concentration of Mg(ClO₃)₂: 352.0 g dm⁻³, electrolyte pH: 6.00
 Temperature: 333 ± 1 K, cathode current density: 32 A dm⁻²
 Cathode peripheral velocity: 40 m min⁻¹
 Theoretical quantity of electricity passed: 100 A h



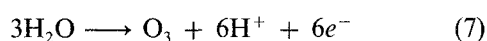
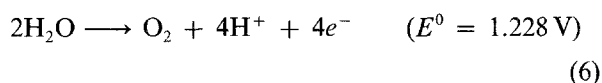
According to the second mechanism, the primary step is the direct discharge of chlorate ion at the anode with the formation of free chlorate radical, which then reacts with water to form perchlorate [10, 12].



However, under alkaline conditions, the formation of perchlorate, may take place as follows, [13]



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



In addition to the loss reactions, Equations 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 perchlorates.

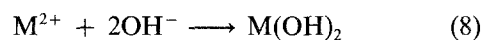


Table 3. Effect of cathode current density on current efficiency for the preparation of magnesium perchlorate

| S. No. | Cathode current density/A dm ⁻² | Voltage/V | Final concentration /g dm ⁻³ | | Loss of Mg ²⁺ /M | Current efficiency for Mg(ClO ₄) ₂ formation/% | Energy consumption for Mg(ClO ₄) ₂ /kWh kg ⁻¹ |
|--------|--|-----------|---|-------------------------------|-----------------------------|---|---|
| | | | ClO ₃ ⁻ | ClO ₄ ⁻ | | | |
| 1 | 19.00 | 4.9 | 15.0 | 365.0 | 0.22 | 70 | 3.40 |
| 2 | 32.00 | 6.9 | 15.0 | 350.0 | 0.28 | 67 | 4.90 |
| 3 | 48.00 | 7.2 | 25.0 | 318.0 | 0.35 | 61 | 5.70 |

Concentration of Mg(ClO₃)₂: 352.0 g dm⁻³, electrolyte pH: 6.00
 Temperature: 333 ± 1 K, anode current density: 30 A dm⁻²
 Cathode peripheral velocity: 40 m min⁻¹
 Theoretical quantity of electricity passed: 100 A h

According to the Pourbaix diagram [14] the magnesium hydroxide forms an adherent coating over the cathode surface in the pH range 8.5–11.5.

The standard potentials of Reactions 1 and 6 are close so that oxygen evolution is always an accompanying reaction. Furthermore the influence of pH on the equilibrium potentials for both Reactions 1 and 6 is the same [11] 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.* [10]. Higher concentrations of chlorate inhibit oxygen evolution due to preferential adsorption of chlorate, thereby increasing the current efficiency. The opposing trend with magnesium chlorate electrolysis must be connected with the removal of magnesium as its hydroxide with the corresponding anodic evolution of oxygen. This loss had already been found to be enhanced when Mg(II) concentration was higher than 2 M in the case of electrolysis of magnesium chloride to magnesium chlorate [15, 16].

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 [17].

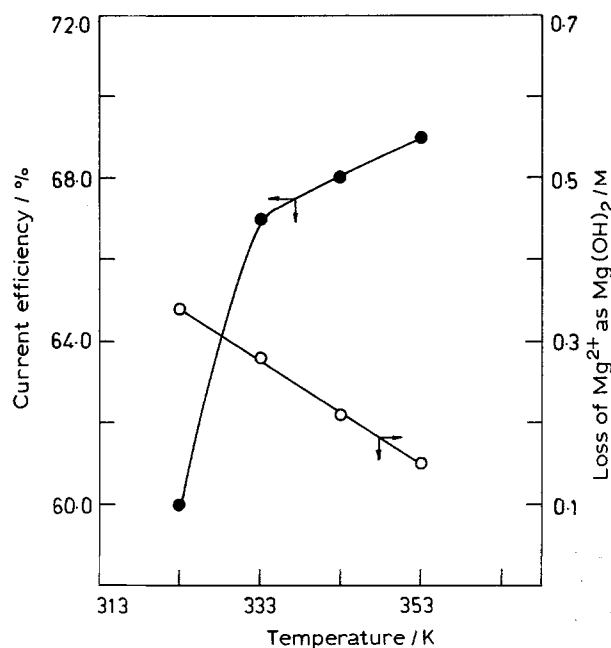


Fig. 2. Variation of current efficiency and loss of Mg^{2+} by precipitation as $\text{Mg}(\text{OH})_2$ with temperature of the electrolyte. Conditions: electrolyte concentration 352 g dm^{-3} , pH 6.0, anode current density 30 A dm^{-2} , cathode current density 32 A dm^{-2} , cathode rotation (peripheral velocity) 40 m min^{-1} and theoretical quantity of electricity passed 100 Ah.

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 increasing the formation efficiency of perchlorate (Reaction 1). This is also true for the electrolysis of magnesium chlorate as observed from the data shown in Table 2. At very low concentrations of chlorate the loss of current efficiency is expected due to Reaction 7. (See Fig. 1). Although the forma-

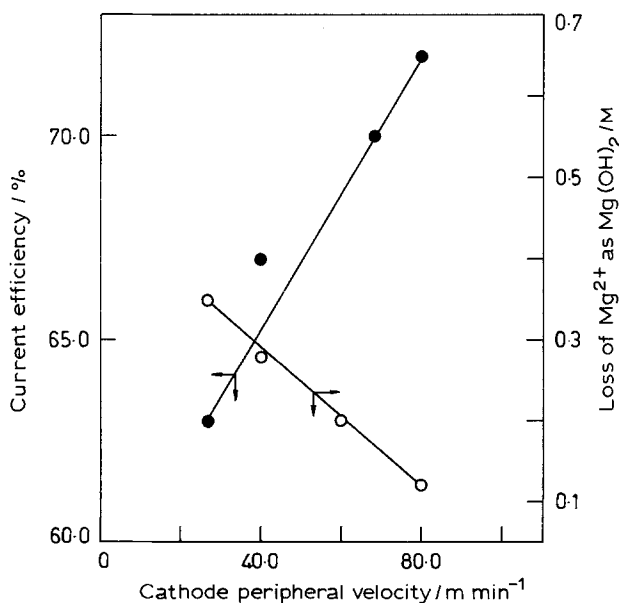


Fig. 3. Variation of current efficiency and loss of Mg^{2+} by precipitation as $\text{Mg}(\text{OH})_2$ with cathode rotation. Conditions: electrolyte concentration 352 g dm^{-3} , pH 6.00, temperature $333 \pm 1 \text{ K}$, anode current density 30 A dm^{-2} and cathode current density 32 A dm^{-2} .

tion of perchlorate is not dependent on electrolyte pH within the specified range [11, 17, 18], in the present case it is true only in a narrow pH region around 6.0. Even though the bulk pH ≥ 7 , the pH of the layer adjacent to the cathode is expected to be more alkaline, [19] thereby favouring preferential precipitation of magnesium hydroxide and consequently loss of current efficiency.

The cathodic loss reaction is the reduction of chlorate and perchlorate when a mild steel cathode is employed. The addition of dichromate or use of a stainless steel cathode inhibits this reaction [17, 20]. For electrolysis of alkaline earth metal chlorates, the additional retarding reaction is the precipitation of their metal hydroxides due to their low solubility. The hydroxide formation depends on the surface pH (pH_s) which is determined by the cathode current density and its rotation. It is found [21] that increasing the peripheral velocity actually produces a slow variation in the value of pH_s , thereby maintaining the pH_s at the desired level as compared to that with slower rotation, i.e. cathode surface pH (pH_s) tending towards bulk pH (pH_b). Figure 3 shows this trend by the increase in current efficiency with cathode rotation rate.

Higher current efficiency with increase of temperature, as observed in Fig. 2, may be due to higher solubility of magnesium hydroxide [9].

5. 100 A. Bench scale experiment

Based on the results obtained on the laboratory scale, a 100 A cell was designed, fabricated and operated for the electrolytic preparation of magnesium perchlorate.

5.1. Experimental details

A stainless steel tank [350 mm (l) \times 250 mm (b) \times 250 mm (h)] fitted with a PVC cover having suitable holes to introduce anode, cathodes, thermometer and the electrolyte acted as the cell. A platinum anode [170 mm (b) \times 180 mm (h)] was used. Two cylindrical stainless steel tubes [75 mm (dia.) \times 210 mm (h)] closed at the bottom and fitted to the two rotating assemblies acted as cathode and were positioned on either side of the anode with an interelectrode distance of 7.5 mm (Fig. 4).

The magnesium chlorate solution obtained from the electrolysis of magnesium chloride was used as electrolyte.

Electrical connection to the cathode was achieved through a mercury contact cup attached to the top end of the rotating shaft driven by a 0.5 h.p. motor. A d.c. current was supplied from a rectifier (0–25 V, 100 A). The electrolysis was carried out until the chlorate concentration was reduced to 5.0 g dm^{-3} .

5.2. Results

The current efficiency obtained in the 100 A cell (Table 4) conforms well with the results obtained at laboratory scale.

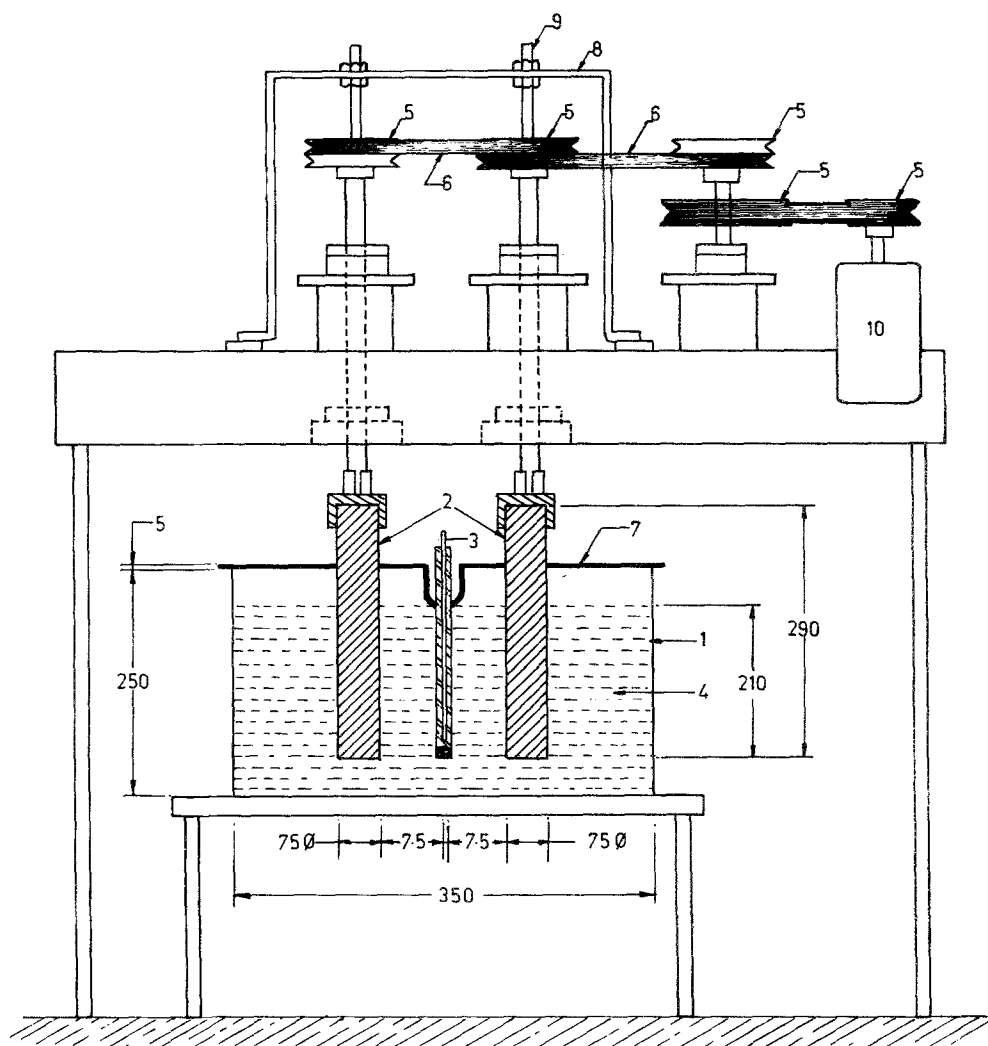


Fig. 4. A sketch of 100 A magnesium perchlorate cell. (Not to scale: all dimensions in millimetres). (1) SS tank, (2) SS cathode, (3) anode, (4) electrolyte, (5) pulleys, (6) V-belts, (7) PVC cover, (8) copper bus bar, (9) mercury cup and (10) 0.5 h.p. motor.

Table 4. Results of 100 A cell for the production of magnesium perchlorate

| | |
|--|------------------------------------|
| 1. Electrolyte | Mg(ClO ₃) ₂ |
| 2. Volume of the electrolyte | 7.5 dm ³ |
| 3. Initial concentration | |
| Cl ⁻ | 0.0 g dm ⁻³ |
| ClO ₃ ⁻ | 352.0 g dm ⁻³ |
| ClO ₄ ⁻ | 0.0 g dm ⁻³ |
| 4. pH | 6.00 |
| 5. Temperature | 333 K |
| 6. Cathode peripheral velocity | 82 m min ⁻¹ |
| 7. Final concentration | |
| ClO ₃ ⁻ | 5.4 g dm ⁻³ |
| ClO ₄ ⁻ | 451.0 g dm ⁻³ |
| 8. Current passed | 100 A |
| 9. Anode current density | 30 A dm ⁻² |
| 10. Cathode current density | 20 A dm ⁻² |
| 11. Total quantity of electricity | 2247 A h |
| 12. Average voltage | 6.00 V |
| 13. Current efficiency for magnesium perchlorate formation | 72.0% |
| 14. Energy consumption for magnesium perchlorate | 3.40 kWh kg ⁻¹ |

6. Conclusion

The electrochemical oxidation of magnesium chlorate to perchlorate can proceed efficiently, when 2 M Mg(ClO₃)₂ (pH 6.0) is electrolysed at an anode current density of 30 A dm⁻² and a cathode current density of 20 A dm⁻² with a cathode peripheral velocity of 82 m min⁻¹ to achieve current efficiency of 72% corresponding to an energy consumption of 4.5 kWh kg⁻¹ of Mg(ClO₄)₂.

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