# MOLTEN SALT ELECTROLYSIS OF MgCl$_2$ IN A CELL WITH RAPID CHLORINE REMOVAL FEATURE

Gökhan Demirci[1], İshak Karakaya[2]

[1]ASELSAN Inc.; Çankırı Yolu 7.km; Akyurt, Ankara, Turkey
[2]METU; Universiteler Mah. Dumlupınar Blv. No:1; Ankara, 06800, TÜRKİYE
Keywords: Magnesium, Molten Salt Electrolysis, Magnesium Chloride

## Abstract

An experimental electrolytic magnesium production cell was designed to remove chlorine gas from the electrolyte rapidly and demonstrate the beneficial effects of reduced chlorine dissolution into the molten salt electrolyte. The back reaction that is the main cause of current losses in electrolytic magnesium production was reduced as a result of effective separation of electrode products and decreased contact time of chlorine gas with the electrolyte. Moreover, smaller inter electrode distances employed and lower chlorine gas present on the anode surface made it possible to work at low cell voltages. Electrolytic cell was tested at different current densities. Energy consumption of 7.0 kWh kg$^{-1}$ Mg that is slightly above the theoretical minimum, 6.2 kWh kg$^{-1}$ Mg, at 0.68 Acm$^{-2}$ anodic current density was achieved for a MgCl$_2$/NaCl/KCl electrolyte.

## Introduction

Magnesium is the lightest structural metal. It is 4.5 times lighter than iron and 1.6 times lighter than aluminum. Magnesium is one of the most abundant elements in the earth. It constitutes about 2% of the earth's crust and it is the third most plentiful element dissolved in seawater with a concentration averaging 0.13% [1]. Despite obvious technical advantages and high abundance, its use is still restricted due to its high production costs that can be attributed to the production methods.

More than half of the magnesium production is carried out by electrolysis. Magnesium production using aqueous electrolytes is not possible because of the highly stable nature of magnesium ions in water. This leaves molten salt electrolysis of MgCl$_2$ as the electrolytic method for magnesium production. On the other hand, pure MgCl$_2$ has a high melting point and magnesium solubility in molten MgCl$_2$ is high enough to lower current efficiencies. Moreover electrical conductivity of the molten MgCl$_2$ is low and its vapor pressure is high. For that reason a chloride salt mixture is used to eliminate these disadvantages.

One of the most important reasons of the high cost is the highly reactive nature of the electrode products, namely magnesium and chlorine. Electrode products react readily when they come into contact and separation of the molten magnesium and chlorine gas has the prime importance to minimize current losses during the electrolysis [2,3,4]. Energy consumption for electrolytic magnesium production is almost double the theoretical value for most efficient industrial cells mainly due to this back reaction.

An energy consumption value of 10-12 kWh kg$^{-1}$ Mg was reported for electrolytic magnesium production, using a high purity MgCl$_2$ feed [5,6,7]. The large difference between the actual and the theoretical, around 6.2 kWh kg$^{-1}$Mg, energy consumptions indicate the possibility of further improvements.

It may be beneficial to have more studies on magnesium production to decrease the gap between the theoretical and the actual energy consumptions. In fact, electro deposition mechanism of magnesium in molten chloride melts has been investigated in considerable detail through the years [8]. However, studies of different electrolysis parameters are scarce for both those representing the industrial production and new designs.

The current losses result from direct contact of the electrode products and back reaction. The investigations of the reaction between dissolved species may help to enhance the cell performance.

Chlorine diffusion was found as the limiting step in recombination reaction between dissolved electrode products in magnesium cell electrolyte [9,10,11]. Thus, it may be possible to reduce back reaction further if the chlorine gas can be removed from the melt in a shorter period of time, considering the fact that the dissolution of the chlorine is proportional to its residence time inside the melt. Current efficiency values are expected to be improved upon decreasing chlorine dissolution into the electrolyte as a result of less interaction of chlorine with the electrolyte.

Therefore, an experimental cell that features rapid chlorine gas removal was constructed. This enabled the removal of chlorine gas with minimized interactions with the floating magnesium metal. Furthermore, it reduced the chlorine dissolution into the electrolyte considerably. Therefore, back reaction was restricted to dissolved magnesium metal and chlorine gas within the melt or fine suspended magnesium particles that might enter the anode compartment due to convection.

## Experimental Details

An externally heated quartz vessel was used to accommodate cell components as in the case of previous studies [9,10]. Electrode leads were extended out of the Teflon lid of the quartz vessel that was placed into a vertical tube furnace. Cell vessel was provided with argon gas flow to create positive pressure inside the cell vessel.

Graphite anode extension rod was placed into a quartz tube which was at the center of the quartz vessel and alumina crucible placed at the bottom. Anode geometry and the quartz tube surrounding the anode made it possible to remove chlorine gas that was produced on the anode surface, from the cell environment, rapidly. The direction of movement of chlorine gas in the cell can be seen by an arrow in anode compartment of Figure 1.

Cathode was designed as circular around the anode and made up of 18 mm wide and 0.2 mm thick electropolished stainless steel ribbons. Windows were opened on stainless steel ribbons by electrochemical machining to increase cathodic current density levels for this setup. One stainless steel rod was spot welded to

the cathode to make electrical connection of the cathode. An alumina tube was used to cover cathode lead.
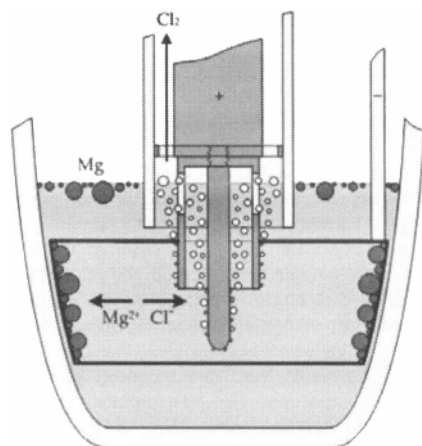


Figure 1 Schematic drawing of the electrolysis cell.

Initial electrolyte composition was; 20% $MgCl_2$, 39.5% KCl, 39.5% NaCl and %1 NaF by weight. $MgCl_2$ obtained from Aldrich had 98% $MgCl_2$ and 1.5% $H_2O$ content. 99.8% NaCl and KCl and reagent grade NaF were from Merck. Electrolysis experiments were carried out at 700°C. Experiments were carried out galvano-statically and cell voltage readings were taken by a portable multimeter and a data acquisition system.

After each experiment, cathode was washed to dissolve adhered salts in the shortest time possible. The cathode was then dried with oil-free compressed air. The cathode weight was recorded and then magnesium deposited to the cathode surface was dissolved in water. A few HCl droplets were added to water to increase the dissolution rate [12]. The amount of magnesium attached to the cathode was determined form the weight difference of the cathode before and after dissolving the magnesium.

After being crushed in a mortar, frozen electrolytes were milled for 24 hours in a rotating glass jar with stainless steel rods inside. Large magnesium particles were collected into a glass cup that was covered with a 50 mesh synthetic fabric. Then the glass cup was flushed with tap water through the fabric to dissolve the salt. Magnesium particles were then dried by applying compressed air to glass cup through the fabric.

Smaller particles, on the other hand, were just subjected to compressed air after milling to prevent their loss in water. The quantities of magnesium attached to the cathode and collected from the frozen electrolyte were added to determine the current efficiency. Pieces of magnesium metal, collected from different parts of cell, are shown in Figure 2.
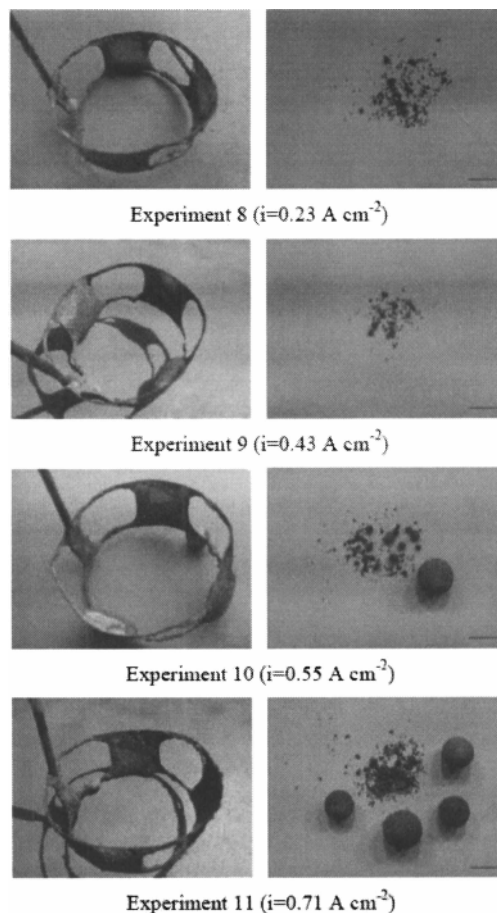


Figure 2 Cathodes and magnesium particles from experiments at different cathodic current densities (the length of the line is 10mm).

**Results and Discussion**

Full details of electrolysis experiments and the results given elsewhere [13] are summarized in Table 1. The net cell voltage vs. time for 13 and 20 mm ACD at indicated anodic current densities are given in Figures 3 and 4 respectively. The net cell voltage was found by subtracting voltage drop along electrical connections from the measured cell voltage. The average net cell voltage is the average of the cell voltage readings after the initial 10 minutes. Anode-Cathode Distance, ACD, is average separation distance between the electrodes before magnesium deposition. The energy consumption, EC, per kilogram of magnesium was calculated from;

$$EC = \frac{E_{average\,net} \cdot 100}{0.4534 g A^{-1} h^{-1} \cdot \%CE} \tag{1}$$

where,

$$0.4534 g A^{-1} h^{-1} = \frac{3600 \frac{second}{hour} \cdot \frac{24.305}{2} \frac{g}{g.equivalent}}{96485 \frac{coulomb}{g.equivalent}} \qquad (2)$$

**Table 1** Summary of the experimental details and the results obtained.

| Experiment | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| $j_{anode}$, Acm$^{-2}$ | 0.68 | 0.90 | 1.32 | 1.32 | 1.75 | 2.18 |
| $j_{cathode}$, Acm$^{-2}$ | 0.24 | 0.31 | 0.43 | 0.44 | 0.58 | 0.77 |
| $V_{avg.\ net}$, V | 3.03 | 3.06 | 3.27 | 3.26 | 3.42 | 3.50 |
| CE, % | 96.0 | 95.1 | 95.1 | 94.4 | 91.1 | 90.3 |
| EC, kWh kg$^{-1}$ | 7.0 | 7.1 | 7.6 | 7.6 | 8.3 | 8.6 |
| ACD, mm | 13 | 13 | 13 | 13 | 13 | 13 |

| Experiment | 7 | 8 | 9 | 10 |
|---|---|---|---|---|
| $j_{anode}$, Acm$^{-2}$ | 0.71 | 1.31 | 1.71 | 2.20 |
| $j_{cathode}$, Acm$^{-2}$ | 0.23 | 0.43 | 0.55 | 0.71 |
| $V_{avg.\ net}$, V | 3.19 | 3.46 | 3.65 | 3.76 |
| CE, % | 99.1 | 97.7 | 98.5 | 97.0 |
| EC, kWh kg$^{-1}$ | 7.1 | 7.8 | 8.2 | 8.6 |
| ACD, mm | 20 | 20 | 20 | 20 |

Current efficiencies above 90% can easily be achieved for all the tests performed in this study as seen in Table 1, despite the quite short inter-electrode distances employed. The level of current efficiencies obtained is an indicative of good separation of magnesium metal and chlorine gas during the electrolysis. Current efficiency decrease with increased anodic current density is pronounced for smaller ACD experiments.

A rapid initial rise in cell voltage was followed by a decrease in 13 mm ACD, forming a peak as shown in Figure 3. Then the cell voltage remained constant or decreased slightly until the end of the experiments. Both the magnitude of the peak and voltage relaxation rate at the latter portion was pronounced at higher current densities. Similar behavior, but to a less extent, was observed for 20 mm ACD, Figure 4.
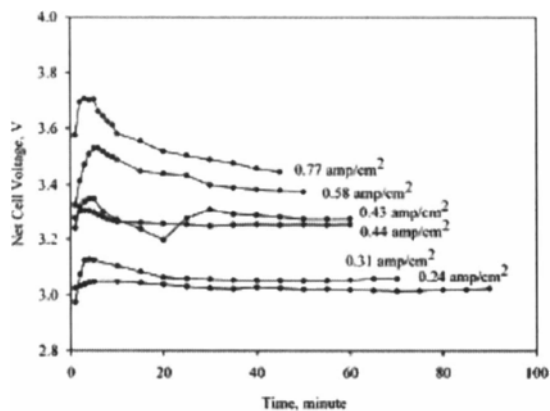


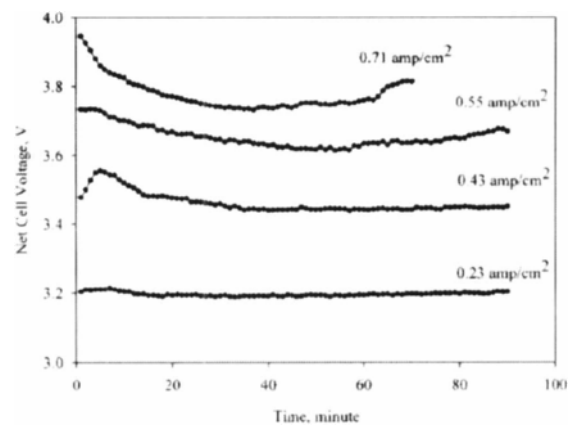Figure 3 Net cell voltage vs. time at 13 mm ACD.



Figure 4 Net cell voltage vs. time at 20 mm ACD.

Characteristic peaks at the beginning of the voltage-time graphs of the experiments are related with the energy required for nucleation. The area under the peaks increased with the increase in current density due to the larger number of nucleation sites.

The final portions of the individual curves were under the control of composition change in general. Voltage relaxation after the initial peaks was due to the decrease in IR drop as a result of the decrease in effective ACD by the magnesium deposition at the cathode surface and increase in electrical conductivity of the melt by the composition change. Cell voltage started to increase at the final portions of the curves due to the dominant effect of decrease in MgCl$_2$ activity when the MgCl$_2$ depleted too much.

The theoretical energy consumption was calculated as 6.2 kWh for present experimental conditions. The computation involves the use of 2.76 V theoretical decomposition potential which was obtained from 2.514 V standard decomposition potential [14] and MgCl$_2$ activity of 0.0025 for the electrolyte [15]. In fact, it is desirable to operate the cell at a voltage higher than theoretical decomposition voltage to supply heat energy required for endothermic MgCl$_2$ decomposition. From the thermo-neutral voltage, which is calculated using the enthalpy change of MgCl$_2$ decomposition reaction, energy consumption of about 7 kWhkg$^{-1}$ was obtained [16]. Furthermore, additional heat must be supplied to compensate the losses from the cell in practice.

As it can be seen in Figure 5, 7.0 kWh kg$^{-1}$ Mg of electrical energy was consumed, at 0.68 Acm$^{-2}$ and 0.24 A cm$^{-2}$ anodic and cathodic current densities respectively for an inter-electrode distance of 13 mm. It is slightly higher than the theoretical value 6.2 kWh for these experimental conditions and well below the lowest energy consumption values industrially practiced, 10.5 to 11.5 kWh kg$^{-1}$ Mg [7].
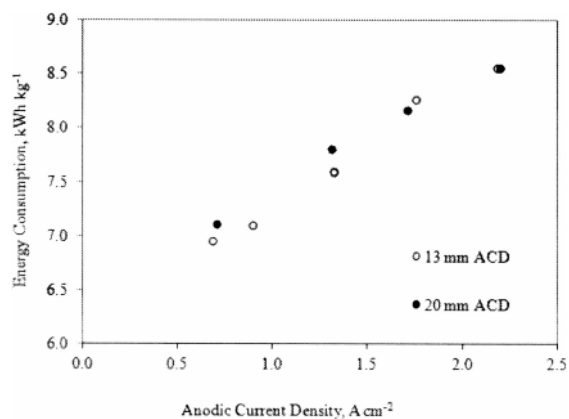
Figure 5 The effect of current density on energy consumption.

There is a small increase in energy consumption with decrease of ACD from 20 mm to 13 mm. This was attributable to the increased turbulence inside the electrolyte with decrease in ACD, since magnesium becomes more susceptible to back reaction when entrapments of chlorine gas or transportation of magnesium occur.

## Conclusions

The cell operates at a low potential due to the low ACD. As a result, 7.0 kWh kg$^{-1}$ Mg was consumed at 0.68 Acm$^{-2}$ anodic current density that is slightly higher than the theoretical value of 6.2 kWh.

The cell demonstrated that, effective separation of electrode products and reduced chlorine diffusion in to the melt due to rapid chlorine removal from the cell made it possible to work with small inter electrode distances and high current efficiencies.

## Acknowledgments

## References

1. Wilson C. B., Claus K. G., Earlam M. R., Hillis J. E., in Kirk-Othmer Encyclopedia of Chemical Technology 4th ed., vol. 14, Wiley, New York, 1995, p. 622.
2. M. Güden, İ. Karakaya, J. Appl. Electrochem. 24 (1994) 791–797.
3. R. Sharma, in: M. Avedesian, R. Guilbault, D. Ksinsik (Eds.), Light Metals 1996, The Metallurgical Society of CIM, Montreal, Canada, 1996, pp.1113–1122.
4. R. Sharma, Electrolytic production process for magnesium and its alloys, US5593566 (1997).
5. H.E. Friedrich, B.L. Mordlike: Magnesium Technology, Springer, Berlin, 2006.
6. R.L. Thayer, R. Neelameggham: JOM, 2001, vol.53, no.8, pp.15-17.
7. P.Ficara, E.Chin, T.Walker, D.Laroche, E.Palumbo, C.Celik: CIM Bulletin, .91, no 1019, April 1998, pp.75-80.
8. A.M. Martinez, B. Borresen, G.M. Haarberg, Y. Castrillejo and R. Tunold: Journal of Electrochemical Society, 151 (7), C508-C513, (2004).
9. G. Demirci, İ. Karakaya: Journal of Alloys and Compounds, 439 (2007) 237–242.
10. G. Demirci, İ. Karakaya: Journal of Alloys and Compounds, 465 (2008) 255-60.
11. G.Demirci, İ. Karakaya: EPD Congress 2011, 597-604 (TMS 2011 Annual Meeting & Exhibition, 2011 San Diego, California).
12. G.Song, A.Atrens, D. St John, X. Wu and J. Nairn: Corrosion Science, 1997, vol. 39 (10-11), pp.1981-2004.
13. G. Demirci, "Electrolytic magnesium production using coaxial electrodes" (Ph.D. Thesis, Middle East Technical University, Ankara, 2006).
14. İ. Karakaya, W.T. Thompson, Canadian Metallurgical Quarterly, 25 (1986) 307-317.
15. E.I. Savinkova, R.P. Lelekova, Zhurnal Prikladnoi Khimii 51 (1978) 1453–1456.
16. İ. Karakaya, "Electrochemical determination of thermodynamic properties of magnesium cell electrolyte: the system MgCl$_2$-NaCl-CaCl$_2$" (Ph.D. thesis, McGill University, Canada, 1985).