CURRENT TRENDS TOWARDS ENERGY REDUCTION IN ELECTROLYTIC MAGNESIUM PRODUCTION

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The specific energy consumption for magnesium metal extraction which had been once around 20-22 kWh per kg, has been brought down to nearly 13-14 kWh per kg, in recent years by employing newer cell designs like modular cell. Yet there appears to be further scope for energy reduction, since the thermodynamic energy requirement is only about 6.5 kWh per kg. In further pursuit of energy economy, the importance of many factors like electrolyte circulation, electrolyte composition, current density, effective separation of anode and cathode products have been identified. New cell designs like bipolar or multipolar type cells have been experimented which claim to be successful enough by bringing down the energy consumption to the desired level of 10 kWh per kg. of magnesium metal.

INTRODUCTION

It is well known, that, the electrolytic production of magnesium by fused salt electrowinning accounts for about 80% of total world production of this metal, the other major process being metallothermic reduction of the oxide by ferro silicon. The chloride cells began to work industrially between 1920 and 1930 and since then much had progressed in the technology of magnesium metal production [1].

Even though the basic principle of magnesium electrolysis was well known, the exact design and operating conditions are, for most part, closely guarded proprietory within producing companies. Three basic types of electrolytic cells are described in literature. They are the Dow cell used by the Dow Chemical Company, USA, the I G Cell based on I G Farben design whose various modified versions are used by companies like Norsk Hydro of Norway and the diaphragmless cell used in Soviet Union. The Dow cell has provisions for external heating and the cell feed used is partially dehydrated magnesium chloride with 1.5 moles of water. The I.G. cell is a refractory lined oblong cell with anodes and cathodes separated by the refractory partitions. The diaphragmless cell is also a refractory lined cell but by eliminating the refractory partitions it is able to provide a large working space leading to increased specific magnesium output [2].

Factors determining the energy consumption

In an electrolytic cell for magnesium production, the specific energy consumption is given by the formula

$$N = \frac{V}{0.454\eta}$$

where N is the specific energy Watt hr/gm, V the electrolyser voltage (Volts) and η is the current efficiency. For a given cell design the cell voltage and the current efficiency are functions of the inter electrode distance, current density, electrolyte composition, temperature and electrode height. Thus these parameters are mainly responsible for determining the energy expenditure for the electrolysis. The current efficiency increases with increased current densities and inter electrode distance thereby decreasing energy consumption. However under these conditions the voltage drop in the electrolyte increases with consequent increase in energy expenditure [3]. Thus it becomes clear that the energy expenditure for the electrolysis can be minimised by finding the most favourable conditions offering minimum cell voltage and maximum current efficiency.

The inter electrode distance is the major factor in increasing the cell voltage. In all the earlier cell designs emphasis was given to keep the anode and cathode products apart by increasing the inter electrode distance. This automatically contributed to the increase in the I.R.drop across the electrolyte reducing the energy efficiency of the cell. However in recent times the theory of mechanism of metal losses during electrolysis had undergone substantial changes. The earlier cell designs have not given much consideration to the pattern of electrolyte circulation and gas lift action of chlorine. It was also believed, a more intensive circulation caused higher metal losses and decreased the current efficiency. But recent theory of physicochemical properties of the electrolyte indicates that the metal losses are mainly caused not by the dissolution of the metal off the cathode surface and its transference through the diffusion layer next to cathode to the anode, but rather by the dissolution of the surface of a large number of magnesium droplets which circulate in the electrolyte and also by the direct interaction of such small metal droplets with chlorine gas evolved at the anode. Hence it became clear that metal losses could be minimised by increasing the sizes and reducing the number of droplets afloat in the electrolyte by ensuring their effective coalescence and their speedy removal from the reaction zone. This

could be achieved by having the electrolyte composition so that surface tension is maximum with respect to cathode and also by utilizing the hydrodynamic forces created by the chlorine evolution for pushing away the metallic globules from the reaction zone to a collection chamber, within the electrolytic cell. Contrary to the previous expectation, the reduction in the inter polar gap could prove beneficial in maintaining reasonable current efficiency with the added advantage of reducing the cell voltage and consequently the energy consumption considerably [3, 4].

Electrolyte specification

An efficient composition of electrolyte for any forms need be selected from the triple systems $MgCl_2$-NaCl-KCl. It has been shown that additions of alkaline earth metals appear to have an unfavourable effect on the electrolytic process. Slurry formation is increased leading to slurrying of the cathode, combustion of metal, increased viscosity of electrolyte, reduction of its actual electrical conductivity, etc. In the development of new composition of chlorine electrolytes, in particular with lithium chloride content, it can be proved that the rational composition of the electrolyte will be selected from the system $MgCl_2$-NaCl-KCl. The composition of the electrolyte has a significantly stronger effect on the current efficiency than the distance between electrodes, anode height and electrolyte temperature. The high surface tension of the electrolyte, at the boundary, with the cathode, is due to the poor wettability of molten salts and consequently a good coating of magnesium to form large droplets.

It was established that one of the major causes for the loss of magnesium is accounted by the combustion of magnesium metal at the surface of the electrolyte in atmospheric air or gaseous chlorine. This is due to a greater density difference between the bath and molten magnesium. The density difference should be minimum so that a major portion of the metal is covered by the electrolyte and not disturbed by the turbulence of the electrolyte. The protecting oxide film is not disturbed under such conditions and prevents the metal from burning. The density difference between the electrolyte and the molten metal at the temperature of electrolysis is recommended to be in the range of $0.03 - 0.08$ g.cm^{-3} [5].

Purification of the feed is also an important factor to obtain good current efficiencies. A whole range of impurities present in the feed constitute a threat, because of their passivation effects upon the electrodes. Magnesium chloride purification should be a combined process including electrochemical and chemical purifications, vacuumming and allowing the metal to stand. A number of impurities (Fe and Ti in particular) adversely affect the electrolysis process only in the presence of 'bond' moisture (in the form of Mg(OH)Cl and magnesium oxide. It has been proved experimentally that vacuumming helps both to break down and eliminate magnesium hydroxy chloride and coagulate the magnesium oxide, which promotes the subsequent rapid setting of the latter. Preliminary elimination of Mg(OH)Cl reduces the amount of MgO (the principal constituent of the passivating film) on the cathode by three or four times [6].

Dispersion of magnesium is the result of film formation on the drops of magnesium from magnesium oxide and other impurities. Sodium fluoride or more commonly calcium fluoride (fluorspar) is used to remove the oxide film over the metal surface and allowing the metal droplets to grow. Simultaneously the viscosity and freezing point of the melt are also considerably reduced. A study on the effect of current efficiency reveals that maximum current efficiency can be obtained if fluorspar content in the melt is around 1 to 1.4% and above this concentration affects adversely the current efficiency [7].

It can be summarised that the electrolyte should satisfy the following requirements in order to obtain a high current efficiency, minimum shunt voltage and reduced slurry formation. (1) The temperature at the start of the primary crystallisation to be 75-100° below the melting point. (2) High electrical conductivity (3) Low viscosity (high flowability)- for the best separation of magnesium from electrolyte and rapid settling of slurry.(4) The density difference between the electrolyte and magnesium at the temperature of electrolysis is in the range of 0.03-0.08 g.cm^{-1}. (5) Minimal slurry formation i.e. minimal tendency to hydrolysis at a reasonable rate of chlorination of magnesium oxide by anode chlorine. (6) Low resistance of electrolyte components.

Current density

Design of electrolytic cell for magnesium depends on the choice of optimum current density which can only lead to the sizing of the cells based on geometrical dispositions. Optimum current density has to be based on techno-economic considerations and energy utilisation aspects. It has been shown that the present international practice of operating the cells at current densities ranging from 0.6 to 0.7 A.cm^{-2} is justified both from techno-economic consideration and energy utilisation aspects [8].

Current density plays an important role in increasing the current efficiency and the wetting properties of magnesium metal. Both the current efficiency and the extent of wetting increased with increase in current densities upto 1.2 A.cm^{-2}. Superwetting by magnesium at high current densities clearly suggests that the well wetted substrates facilitate the growth of electrodeposited magnesium to form bigger balls prior to detachment from the cathode substrate and increase the current efficiency. Equally important is the influence of anodic current density. The rate of chlorine evolution and the size of chlorine bubbles depend on the anodic current density and change the mass transfer conditions within the electrode gap. Heat balance at high current densities would unfortunately be a problem. More work in commercial cells or cells that simulate the hydrodynamic conditions of the commercial cells is to be carried out to further optimize the maximum current density for magnesium cells [9].

New cell designs

In diaphragm cells, ordered circulation of electrolyte with good current efficiency is possible. But in diaphragmless cells the current efficiency is somewhat less due to the path followed by magnesium droplet from electrochemical compartment to the metal collection chamber being always longer compared to the diaphragm cell. Hence it becomes clear that the priority should be given while designing the diaphragmless cells for more orderly and controllable circulation of the electrolyte. Thus more stress on the study

of hydrodynamic conditions and gas lift action of the electrolyte have attained greater importance in designing the magnesium cells with reduced energy consumption. Studies are also made on the effect of atmospheric humidity on current efficiency [10]. An analysis of the experiments conducted revealed that the amount of magnesium oxide content in the magnesium chloride and in the electrolyte increased with the content of water vapour in the air.

Taking the above factors into consideration, newer cell designs have come into existence. The modular cells designed by Central Electrochemical Research Institute, Karaikudi have brought down the energy consumption to 13 kWh.kg^{-1} of magnesium. In this design, provision to take advantage of the gas lift action of chlorine has been made by narrow inter-polar gap and at the same time provision for free circulation of electrolyte between electrolytic and nonelectrolytic zones has also been made so that the entire cell temperature could be maintained at desired level. The hydrodynamic force due to chlorine evolution pushes out the magnesium metal formed to a tranquil nonelectrolytic zone within the cell. A prototype 30 KA cell has been successfully operated. Similar cells have been set up in a 600 T per year commercial magnesium plant of the Tamilnadu Government. Though Dow Chemicals Company and other producers have also succeeded in bringing down the energy consumption in the commercial cells, yet there are more pursued efforts in this direction to bring down the energy consumption still further.

Bipolar cells

The development of bipolar cells by Alcoa for the production of aluminium has prompted investigations on the possibility of similar designs for magnesium cells. Considerable work on the anode-cathode configuration had indicated, that a narrow anode/cathode distance could be used to advantage for further reduction of the unit power consumption. However, problems and uncertainties stood in the way of adopting this attractive configuration. The basic problem was the excessive heat extracted by the electrodes especially by the graphite anodes in relation to the reduced internal heat generation. The most direct way to obviate this problem was to make multiple flow of current in and out of the cell, i.e. adopt a multipolar cell design.

The principle is simple. If an electrically conducting plate is inserted between anode and cathode of a conventional electrolytic cell, the side of the plate facing the anode becomes cathodic as the current passes through the plate. The other side becomes anode. The plate functions therefore as a bipolar electrode and thus the productivity of the cell is nearly doubled. The reason that production is not exactly doubled is that some current bypasses the bipolar plate. One can reduce the extent of this bypass current by confining the plate between electrically insulated walls. But this loss may never be completely eliminated, because one needs to provide passages for the circulation of the electrolyte. Careful design [11] reduces this loss of current efficiency which becomes one of the limiting factors to the process of inserting additional bipolar plate between anode and cathode to further increase productivity. Intermediate bipolar electrodes used in this are valuable in that they increase the effective cathode area on which metal formation can take place, without increasing the heat and power losses involved by providing large number of external electrical connections.

An optimum cell design results by having a number of bipolar electrodes disposed in series in the path of the electrolytic current between anode and cathode. As the total cell amperage could not usually be accommodated within the size of the bipolar plate, the arrangement can be repeated in a mirror image path from the other face of anode towards another cathode for a symmetric electrode assembly and repeated again by installing sufficient electrode assemblies to obtain the total amperage desired. A modular arrangement thus resulted [12]. The average energy consumption was around 11 kWh.kg^{-1} of magnesium metal.

Few patented information reveals about the description of the cell with anode, cathode and intermediate bipolar electrodes with small interpolar gaps. In operation, a mixture of electrolyte, molten metal and gas-typically chlorine-streams upward through the electrolysis regions. The electrolyte-metal mixture spills over each intermediate bipolar electrode, over the cathode and into the duct behind the cathode. The duct extending adjacent to the back face of the cathode includes a restricted passage for electrolyte/metal mixture, preferably at substantially the level of top edge of the cathode. This restricted passage serves to control the flow of electrolyte mixture and prevents metal droplets from returning. The cell contained several electrode assemblies varying from 3 to 8 and each electrode assembly contained bipolar ranging from 1 to 7. The cell was operated between 928 and 968K at current densities ranging from 0.3 to 1.5 A.cm^{-2}. The inter electrode spacing was from 4 mm to 25 mm. Intermediate bipolar electrodes used in this are valuable in that they increase the effective cathode area on which metal formation can take place, without either increasing the heat and power loss involved in providing large number of external electrical connections. One problem which intermediate bipolar electrodes generates is that of current leakage. To mitigate this problem several features are provided in the cell design and operation [12].

Few other patented information also reveals the use of bipolar electrodes for reduced energy consumption [13-15]. These bipolar electrodes consists of a flat graphite portion to provide the anodic face and an iron portion to provide a cathodic face, both materials being spaced from each other and jointed together with rods of iron which are tightly secured to the graphite to ensure an intimate electrical connection. A cavity thus formed between the two materials is arranged to fitly communicate at one end with a through hole in the partition to allow passage of electrolyte bath carrying magnesium metal from the electrolytic chamber to metal collection chamber. The essential features of the electrolytic cells using such bipolar electrodes are: one pair of anode and cathode arranged vertically; at least one intermediate bipolar electrode placed in a row between anode and cathode; an electrolytic chamber to contain the electrodes and a metal collection chamber which is attached to the electrolytic chamber but separated therefrom by a partition.

These cells have used electrolytic bath which has density greater by 0.02 to 0.10 gm.cm^{-3} than magnesium at the operating temperatures employed

and an electrical conductivity of 2.4 $\Omega^{-1}cm^{-1}$. Typically examples of the various baths employed are: (1) 20% $MgCl_2$, 50% NaCl, 30% $CaCl_2$ (by weight) (2) 20% $MgCl_2$, 60% NaCl, 20% KCl, (by weight) (3) 20% $MgCl_2$, 60% NaCl, 10% KCl, 10% LiCl (by weight). A current density of 0.52 to 0.56 $A.cm^{-2}$ was employed. The energy consumption worked out to 9-10 $kWh.kg^{-1}$ of magnesium.

Central Electrochemical Research Institute, Karaikudi, has also initiated some efforts in this respect for developing bipolar cells so as to keep abreast of the latest development taking place in the magnesium technology. The cell was operated in a 500A scale [16]. The individual cell voltage was about 4.0V and the total voltage was about 13V for the three bipolar unit cells. The current density applied was about 1.7 $A.cm^{-2}$. Current efficiency about 65-75% was obtained with an energy consumption of 15-17 $kWh.kg^{-1}$. Judging by the smallness of the cell, there seems to be more scope for further energy reduction in the scaled-up cells since problems regarding the bypass current can be sorted out.

CONCLUSION

The technology of magnesium metal production involves many interrelated complex factors and the improvement made in each aspect contributes considerably to the improvement in the energy efficiency. Several other factors like use of newer cathode materials like titanium boride, zirconium boride etc. may also give better scope for further reduction in energy demand of the process. The understanding of physicochemical properties of the electrolyte and effect of the various impurities are also to be studied.

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