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BIPOLAR CELL FOR PRODUCTION OF MAGNESIUM

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Bipolar type of cells appear to be promising in the field of fused chloride electrolysis as found in the case of ALCOA type aluminium cells. The adoption of this technique for magnesium production could also lead to design of improved type of cells which would result in further cost reduction. CECRI with its experience on building modular cells without the diaphragm has conducted trial experiments on bipolar systems for magnesium production. The preliminary results obtained from a cell of 500 A capacity is discussed.

Key words: Bipolar cell, electrolytic magnesium

INTRODUCTION

Continuous efforts are being made all over the world to reduce the specific energy consumption for the electrolytic production of magnesium to make this metal compete effectively with aluminium as a structural material. Whereas in the cells earlier designed, the specific energy consumption for magnesium was around 22 kWh/kg the development of modern partitionless cells has enabled the energy reduction to about 13-14 kWh/kg. The thermodynamic energy requirement for the production of magnesium being only 6.5 kWh/kg, there is still scope for considerable reduction in the specific energy consumption. Central Electrochemical Research Institute (CECRI) has been engaged in the development of technology for magnesium metal and successful in developing modular type diaphragmless cell wherein the energy consumption has been brought down to 13-14 kWh/kg [1]. The essential feature of this cell is the utilisation of gas-lift principle which is obtained when the electrodes are kept close together. Chlorine gas evolved at the anode enables the vigorous circulation of the electrolyte and helps in the separation of magnesium formed at the cathodes which is pushed away from the electrolytic zone. From the experience gained in such type of cells, some attempts have been made to evolve newer designs which could reduce the energy consumption further. One such line of approach would lie in the development of bipolar systems. It is now known that the success of chloride technology for aluminium which is in an advanced stage of development was mainly due to the bipolar type of cells used by ALCOA [2]. In these cells electrodes are kept very close and the circulation effect produced by chlorine gas is effectively used to get high current efficiency, a principle which appears to be very similar to that adopted in the modular type magnesium cells. It is, therefore, felt that similar bipolar systems could work effectively in the case of magnesium production.

The apparent advantages of bipolar type of cells are considerable savings of resistance losses, simplified bus bar arrangements, high space-time yields and reduced energy consumption. Unlike the aluminium bipolar cells where graphite is used as the bipolar electrodes, in the case of magnesium cells one has to look for a composite bipolar electrode. This is mainly because graphite is not suitable as cathode in magnesium cell, where it is found to disintegrate very fast due to the formation of magnesium carbide. Hence in the case of magnesium chloride electrolysis, the bipolar electrodes should be plates of graphite and iron.

Some earlier work has been done by Dow [3] on such bipolar cells. It consists of built-up graphite carbon slab and an iron plate acting as terminal electrodes. The intermediate bipolar electrodes consist of slabs of graphitised carbon, the cathode face of each block being covered by an iron plate or by electrodeposited iron. The cell consisted of two chambers, an electrolytic chamber and metal chamber divided by a curtain and a pump to circulate the electrolyte. This cell was not ultimately successful.

Work in CECRI on bipolar system was directed towards the development of cells where both the bipolar principle as well as gas-lift principle (which was advantageously utilised in modular cells) could be effectively combined, so that circulation of electrolyte between the electrolytic chamber and the metal collection chamber is obtained without a pump. Initial studies were directed towards evolving proper design of the electrolytic cell, arrangements of electrodes to avoid stray currents which will minimise the bipolar effect, evolving suitable methods for fabricating bipolar grids and a general understanding of the characteristics of the bioplar systems

EXPERIMENTAL

A general arrangement of the 500A cell is given below. The cell essentially consists of a refractory lined vessel 28 x 15 x 40 cm. The thickness of the bricklining was about 10 cm. The graphite plate of 15 x 20 cm placed vertically at rear wall of the cell formed the anode. From the anode first bipolar electrode was placed at a distance of 1.5 cm and second electrode was placed at the same distance from the first plate. A mild steel cathode of identical size was placed at the distance of 1.5 cm from the second bipolar electrode and a free space of 12.5 cm width was provided at the front for metal collection and sludge removal. The free space was also used for positioning AC heating electrodes to keep the electrolyte molten. The electrolyte used was $MgCl_2$ 10-15wt%, NaCl plus KCl 70wt%, $BaCl_2$ 15wt% which is the same as used in the modular type of cells of CECRI.

Initial experiments in the above cell revealed some basic structural deficiencies, some of which relate to positioning of the bipolar electrodes. It was found that when these bipolar electrodes were

fixed to the wall of the cell through two protruding wings on either side, considerable short circuiting developed mainly due to the seepage of the electrolyte into the walls of the cell. This has resulted in loss of current efficiency. The voltage across each of the bipolar electrodes was 4.5, 4.0 and 4.5 V respectively with a total of 13 volts. Unlike the modular cells, bipolar cells require higher current density of the order of 1.7 A/cm^2, since at lower current densities yields were very poor. Based on the experience of the initial designs, an improved bipolar cell was constructed to avoid short circuiting. In this, none of the electrode leads were allowed to touch the outer wall of the cells. The anode lead was introduced to the cell vertically from one end of the cell while the cathode was fixed on the other side, the bus bars running above the cell. Bipolar plates were also positioned by setting them on the grooves at the bottom of the cell with no arms extending through the sides. This improved cell was operated for over 21 days at 500 A rating and about 134 kg of magnesium was produced. The performance data of this cell is given in Table I.

TABLE I: Performance data of bipolar magnesium cell

Current rating (A)	500
Number of bipolar units	3
Current density (A/cm^2)	1.7
Cell Voltage (V)	13 (Total for all the three bipolar unit cells)
Voltage of individual bipolar unit (V)	4.5, 4, 4.5
Inter-electrode distance (cm)	1.5
Average current efficiency (%)	60
Maximum current efficiency obtained (%)	75
Average energy requirement (kWh/kg)	17
Duration of electrolysis (days)	21
Metal collected (kg)	133.7

RESULTS AND DISCUSSION

The principle of the bipolar system is that if an electrically conductive plate is inserted between anode and cathode of a conventional electrolytic cell, the side facing the anode becomes cathodic, as the electrolytic current passes through the plate. The opposite side becomes anodic and the plate functions as bipolar. The productivity of the cell is nearly doubled [4]. If more such plates are introduced say n number of times, the productivity of the cell should increase by (n + 1) times. But in practice the productivity is not exactly increased by (n + 1) times but somewhat less, the reason being that some current bypasses the bipolar plates flowing directly to the cathode. One can minimise the bypass current by confining the plates between electrically insulated walls. But this loss could not be completely eliminated due to the need for provision for circulation of the electrolyte. The calculation of faradaic efficiency in such a system should therefore take this factor also into account. An approximate method of estimating the current efficiency is given below.

If n bipolar plates are introduced between anode and cathode, the total effective cell units will be n + 1. When the input current passed in the cell is I, the effective ampere hours for calculation of faradaic efficiency will be given by

$$\left[\left\{\sum_{n=0}^{n=n}\frac{V_{n\leftrightarrow n+1}-V_d}{R_{n\leftrightarrow n+1}}\right\}+\left\{I-\frac{\sum_{n=0}^{n=n}V_{n\leftrightarrow n+1}-V_d}{\sum_{n=0}^{n=n}R_{n\leftrightarrow n+1}}\right\}\right]\times h$$

where $V_{n\leftrightarrow n+1}$ is the voltage measured between 'n' and 'n + 1' electrodes: V_d the decomposition potential of magnesium chloride in the bath plus the overvoltages; $R_{n\leftrightarrow n+1}$ the resistance of the bath in the compartment between 'n' and 'n + 1'electrodes i.e. $R_{n\leftrightarrow n+1} = (\ell\ l_{n\leftrightarrow n+1})/(A_{n\leftrightarrow n+1})$:$A_{n\leftrightarrow n+1}$ the average surface area of the 'n' and 'n + 1' electrodes; ℓ the specific resistance of the bath; $l_{n\leftrightarrow n+1}$ the interelectrode distance between 'n' and 'n + 1' electrodes; 'h' hours of electrolysis and I the input current in amperes.

The best way of judging the performance of such bipolar cells will be by the specific energy consumption. In the experimental cell mentioned above the specific energy consumption was 17 kWh/kg during the best period of operation which is rather encouraging. By careful design the losses due to leakage current could be reduced which would lead to lowering the energy consumption further.

During the above experiments it was found that a proper method of fastening iron and graphite in making bipolar electrodes is very important. Initially graphite and iron were fixed by using iron screws. This arrangement was found to fail within 2 to 3 days. Hence an improved arrangement consisting of a combination of graphite and iron screws gave better performance. However, it is felt that more sophisticated arrangements are possible by using electroplated coatings or those obtained by metal spraying of iron on graphite.

CONCLUSION

The initial experiments on bipolar systems for magnesium chloride electrolysis indicate that many of the anticipated advantages like higher space-time yield could be possible by adopting the system. By perfecting fabrication technique of the bipolar electrodes and by adopting careful cell designs, the above objective can be achieved.

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