

CATHODE CONDITIONING IN MOLTEN SALT ELECTROWINNING OF MAGNESIUM METAL FROM $MgCl_2$ - $NaCl$ - KCl - $BaCl_2$

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The current efficiency in the electrolytic cells for magnesium depends much upon the wettability of cathode surface by molten metal and the electrolyte. The possibilities of improving cathode conditioning in $MgCl_2$ - $NaCl$ - KCl - $BaCl_2$ systems by marginal adjustments of bath compositions, cathode material and use of addition agents were studied in a laboratory scale and the results are reported.

Key words: Electrowinning Mg, quaternary molten electrolytes, cathodes

INTRODUCTION

It has been recognised that a major factor which affects the current efficiency in the commercial electrolytic cells for magnesium is the wettability of the cathode surface with respect to magnesium and the ability of the metal deposited to grow into a considerable size on cathode surface before getting released from it. Factors affecting these and studies to improve the wettability have already been reported [1]. However, most of these are related to the composition of the mixture of electrolyte used in each case and conditions have to be optimised for each electrolytic system which is employed for commercial scale cells. The quaternary system of $NaCl$ - KCl - $BaCl_2$ - $MgCl_2$ has been adopted in the electrolytic cells developed at CECRI for several reasons described elsewhere [2,3]. The possibilities of improving cathode conditioning in such systems by marginal adjustments of electrolyte composition, cathode material and the use of addition agents were studied in laboratory scale and the results are reported.

Recent studies on the electro-deposition of magnesium metal indicate that the metal losses are mainly caused not by the dissolution of the metal near the cathode surface and its transference through the diffusional 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 evolved at the anode. Hence it becomes clear that the losses could be minimised by increasing the sizes and reducing the number of magnesium droplets afloat through coalescence and their speedy removal away from the zone of reaction. Accomplishment of these could be done by adjusting electrolyte composition so as to have the maximum surface tension with respect to cathode [3,4].

A factor which has much bearing in this context is the wetting angle of the solid iron surface by the electrolyte compared to molten magnesium. An improved wetting of both the surface of the cathode and that of the molten magnesium by the electrolyte is tantamount to the deterioration of the wetting power of the solid cathode surface by magnesium. Surface tension measurements of various multicomponent chloride mixtures reported in literature are worthy with respect to gas-electrolyte interfaces only. Correlation studies [1] on the current efficiency and gas-electrolyte surface

tension have, however, indicated that the latter has an effect on the current yield in the sense that higher current efficiency was obtained when those values which have high surface tension in the gas-electrolyte interface is employed. However, this is only an indirect evidence since it is the surface tension at the solid cathode electrolyte interface which is more relevant. Hence it is desirable to measure the wetting angle of the cathode by magnesium in the presence of electrolyte of different compositions but this is difficult due to several experimental constraints. The best alternative, under these circumstances seemed to be a qualitative observation of the wetting property so that electrolytes and electrodes with optimum surface properties could be chosen for the industrial electrolysis.

EXPERIMENTAL

A small refractory lined cell of inner dimensions 18 x 12 x 12 cms and outer dimensions 25.5 x 20 x 20 cms was constructed to study the deposition of magnesium metal at various operating conditions.

The anode consisted of a 15 x 10 cms graphite plate and the different cathodes of the same size were employed. The effective electrolysis area was about 75 sq.cm. A provision for additional heat requirement by A.C. was also made at one end of the cell.

A cross sectional view of the cell is given in Fig. 1.

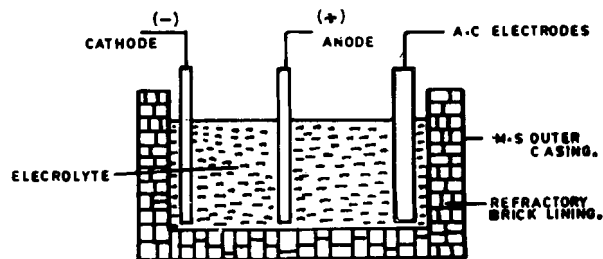


Fig. 1: Magnesium deposition cell

The electrolyte was initially melted by employing A.C. power source at one end of the cell and brought to the desired level of 7.5 cm height. The cathode plate was fixed at the other end of the cell and the anode is fixed at a distance 7.5 cm away from the cathode. Then D.C. was applied and a current of 50A was maintained for a period of 30 minutes. The temperature was maintained at the optimum conditions with the help of AC throughout the period. After 30 minutes of electrolysis the cathode plate was lifted up in such a manner that the deposited metal over the cathode surface is not disturbed and the same is allowed to cool as such in a closed atmosphere. Then the salt crust over the metal deposits was removed and the shapes of the metal deposited over the cathode were examined for different experimental conditions.

Since the condition of metal deposits depends upon the cathode surface, the bath composition and also on the addition of fluorides, a number of experiments were conducted employing variation in each category.

Cathode material

The various materials and their surface characteristics tried in the cathode are given below:

1. Special M S plate (AS 515 Gr 70)
2. Vertical grooved M S plate (IS 226)
3. Chequered grooved M S plate (IS 226)
4. Horizontal grooved M S plate (IS 226)
5. Plain M S cathode plate (IS 226)
6. Stainless steel plate (316)
7. Cast iron plate
8. Cast steel plate (SA 216 Gr WCB)

Deposition of magnesium metal was tried employing all these plates and the appearance and shapes of metal globules deposited over various cathode plates were photographed. A fixed electrolyte of composition NaCl-35%, KCl-35%, MgCl₂ -15%, BaCl₂ -15% was employed. Photographs of the various deposited cathodes are given in Figs. 2 and 3. Results obtained are presented in Table I.

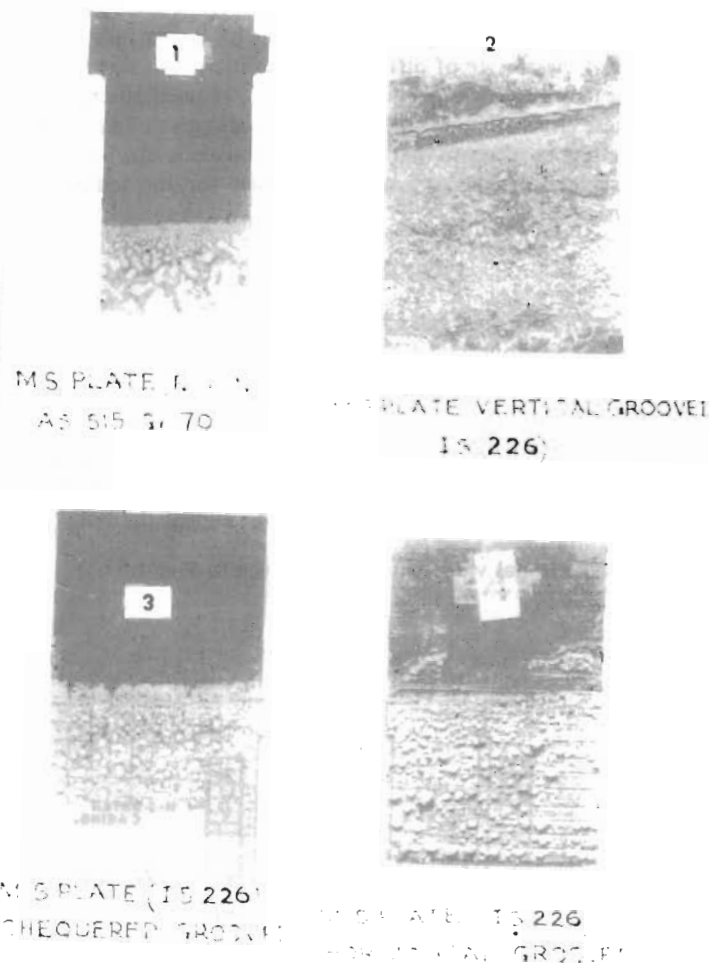


Fig.2: Cathode materials

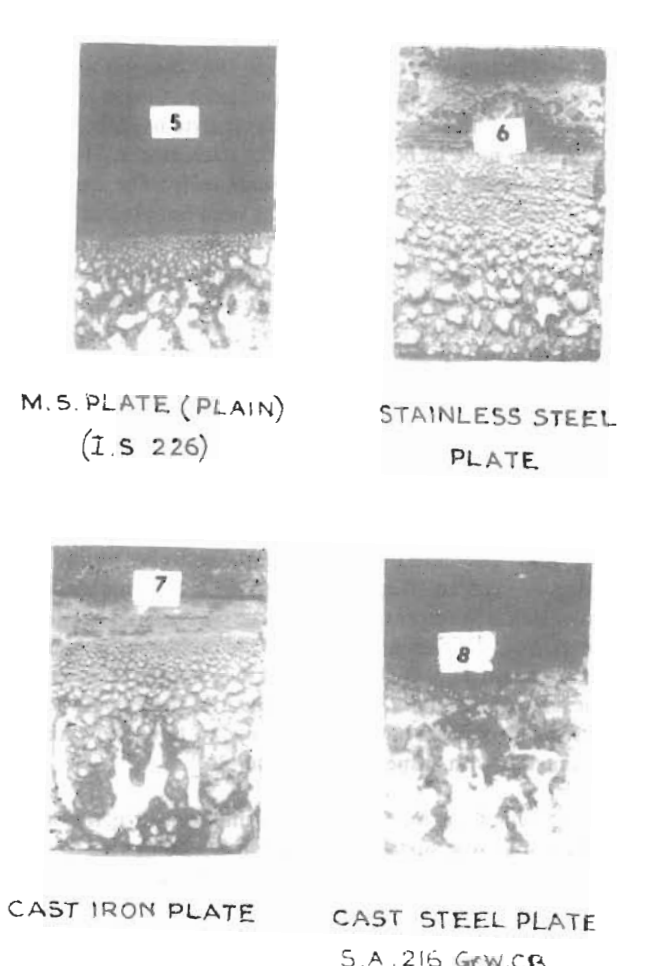


Fig.3: Cathode materials

Table I: Influence of cathode material on the deposition characteristics: Bath composition: (Wt%) NaCl - 35, KCl - 35, BaCl₂ - 15, MgCl₂ - 15 Addition agent: (Wt%) CaF₂ - 2

Sl. No.	Cathode material	Remarks
1.	Steel plate (AS 515 Gr 70)	Tiny globular deposits
2.	Vertical grooved M S plate	Nonuniform deposit over cathode surface in the form of small metallic globules
3.	Chequered grooved M S plate	Uneven distribution of metal deposits
4.	Horizontal grooved M S plate	- do -
5.	M S cathode plate (IS 226)	Bigger metal globules over cathode surface, Deposits more or less uniform.
6.	Stainless steel plate	- do -
7.	Cast iron plate	- do -
8.	Cast steel plate (SA 216 Gr WCB)	- do -

Composition

The second variation that was tried was with respect to the electrolyte composition to find out which composition has the good surface tension and also improves coalescence of the metal. It is reported [1] that the presence of sodium chloride as a major constituent improves the deposition conditions by better coalescence of metallic globules thereby improving the current efficiency. Hence, the following electrolyte compositions were employed for finding out the deposition conditions.

(1) NaCl - 70%; BaCl₂ - 15%; MgCl₂ - 15%

(2) NaCl - 60%; KCl - 10%; BaCl₂ - 15%; MgCl₂ - 15%

(3) NaCl - 35%; KCl - 35%; BaCl₂ - 15%; MgCl₂ - 15%

In all the above cases CaF₂ was added to the extent of 2% by weight of the total electrolyte.

Plain M S plates were employed as the cathode in all the three cases and the electrolysis was conducted for a period of 30 minutes at a current of 50A. After the electrolysis the cathodes were removed and the deposition patterns were photographed.

Fig. 4 gives the deposition pattern of magnesium metal. Results obtained are presented in Table II.

TABLE-II : Effect of bath composition on the deposition characteristics (Cathode material: Mild steel (IS.226) Addition agent: (Wt%) Calcium fluoride 2

Sl. No.	Bath composition (Wt%)	Remarks
9.	NaCl - 70 BaCl ₂ - 15 MgCl ₂ - 15	Deposit in large size metal globules Practical difficulty in the operation of the cell due to higher melting point of the bath (725°C)
10.	NaCl - 60 KCl - 10 MgCl ₂ - 15 BaCl ₂ - 15	Not good and so also the deposit is nonuniform and tiny globular size
11.	NaCl - 35 KCl - 35 BaCl ₂ - 15 MgCl ₂ - 15	Good, sufficiently grown metal globules
12.	- do -	Good. Deposit uniform



NaCl - 70%
BaCl₂ - 15%
MgCl₂ - 15%



NaCl - 60%
KCl - 10%
BaCl₂ - 15%
MgCl₂ - 15%



NaCl - 35%
KCl - 35%
BaCl₂ - 15%
MgCl₂ - 15%

Fig.4: Bath composition

Addition agents

It is known that the addition of fluorides in small quantities improves the deposition by enhancing the surface tension of

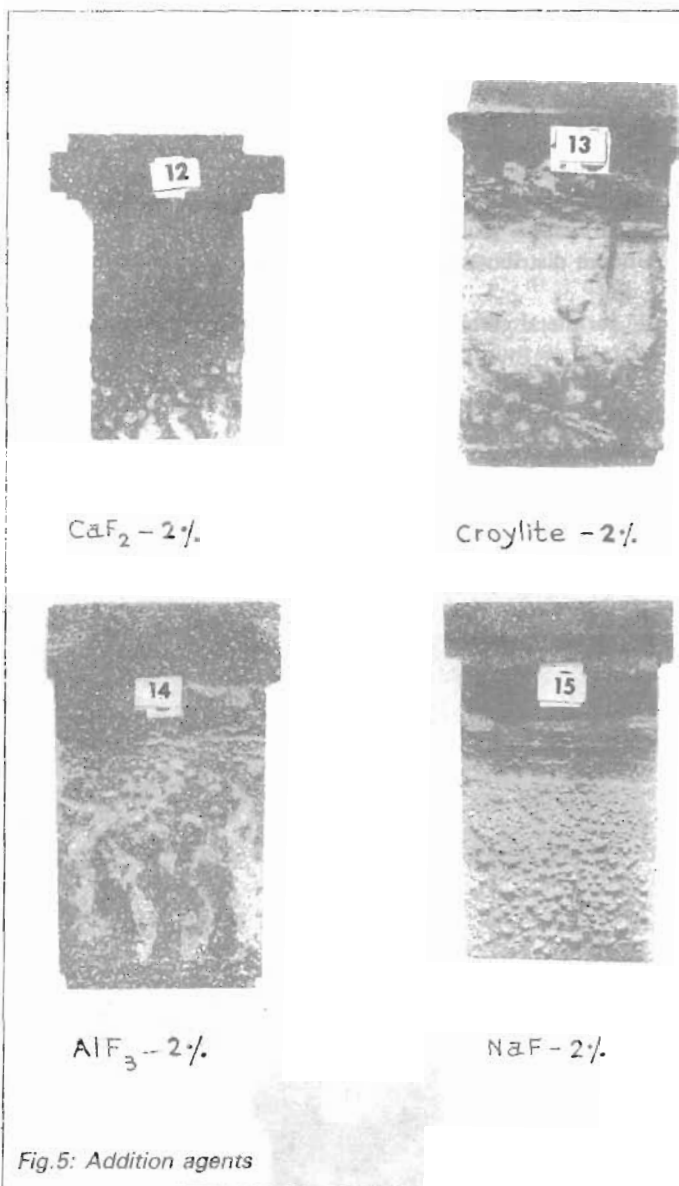


Fig.5: Addition agents

TABLE-III : Effect of addition agents on deposition characteristics
Bath composition: (Wt%) NaCl - 35, KCl - 35, BaCl_2 - 15, MgCl_2 - 15

Cathode material: Mild steel (IS.226)

Sl. No.	Addition agent (Wt%)	Remarks
13.	Cryolite 2	Uniform plating on cathode surface but globular growth of metal is not found
14.	Aluminium fluoride 2	Uniform coating and very big globules of metal are formed over cathode surface
15.	Sodium fluoride 2	Tiny globules of metal over cathode surface and deposit in non-uniform pattern

the electrolyte and thereby increasing the wettability of electrode with respect to magnesium [4,5]. The fluorides also dissolve the oxide film over the droplets of metallic magnesium and improve the coalescence. Various fluorides, besides CaF_2 , such as cryolite, aluminium fluoride, and sodium fluorides were tried to select the best one for deposition conditions over M S plain cathode plates. The bath composition was maintained the same at 35% NaCl, 35% KCl, 15% BaCl_2 and 15% MgCl_2 and the fluorides were added to the extent of 2% in each experiment.

Fig. 5 shows the deposition characteristics of magnesium metal after 30 minutes of electrolysis employing different addition agents. Results are presented in Table III. RESULTS AND DISCUSSIONS

Of the several variations tried in respect of cathode material, bath composition, fluoride addition etc. the most favourable conditions have to be selected for obtaining best results.

It is found that out of several cathode plates the following are found to give better deposition conditions:

1. M S plates (IS 226) 5 of Fig. 3
2. Stainless steel plate (316) 6 of Fig.3
3. Cast iron plate 7 of Fig. 3
4. Cast steel plate (SA 216 Gr WCB) 8 of Fig.3

Since the use of stainless steel plate may result in the inclusion of impurities like Ni and Cr with deposited metal, its usage is not advisable. Hence plain M S cathode or cast iron or cast steel plates can be used as cathodes without much detriment to the purity of deposited metal. The use of cast steel may perhaps reduce the cost of fabrication of the cathodes to a considerable extent in large industrial scale operations.

Even though the use of NaCl-rich electrolyte very much favours better deposition conditions (9 of Fig.4), one has to give considerations for certain practical problems that may be encountered while employing such systems in electrolytic cells. For an electrolyte containing 70% - NaCl, 15% - BaCl_2 15% MgCl_2 , the melting point is very high (725°C) and hence the cell has to be operated always at a higher temperature at which the vapour pressure of magnesium is fairly high. This results in considerable loss of metal in the form of vapour and reduces the current efficiency. Moreover, at higher temperatures the tendency for magnesium to burn is more which not only reduces the current efficiency but also increases the sludge formation. The sludge formation in its turn has a number of adverse effects. Tiny metallic globules are entrapped into the sludge and sink to the bottom. This will, after certain period, result in short circuiting the electrodes thereby hampering the electrolysis very much.

It has been found out in practice that it is always better to have the melting point of the electrolyte lower than that of magnesium metal for convenient operating conditions. Bearing these factors in mind it has been found out that an electrolyte containing NaCl-35%, KCl-35%, BaCl_2 -15% and MgCl_2 -15% can be employed for obtaining best results.

Of the various fluorides tried aluminium fluoride and calcium fluoride gave better deposition conditions with the formation of

bigger metallic globules. However, addition of aluminium fluoride invariably results in the contamination of aluminium in the deposited metal.

CONCLUSION

It is concluded that best results can be obtained by employing cathodes made of mild steel (IS 226) or cast steel or cast iron with an electrolyte consisting of NaCl-35%, KCl-35%, BaCl₂-15% and MgCl₂-15% with small additions of CaF₂.

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