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(Received, February 8, 1995

Revised form accepted, May 17, 1996)

## A NEW APPROACH TO CURRENT EFFICIENCY CALCULATION

### IN MAGNESIUM ELECTROLYSIS

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## SUMMARY

Energy consumption in an electrolytic process is mainly governed by current efficiency and voltage efficiency. Hence an accurate calculation of the current efficiency will greatly help in evaluating energy data precisely. An attempt has been made in this study to perfect an alternate method for calculating the current efficiency (C.E.) from the chlorine gas liberated at the anode during magnesium chloride electrolysis. The anodic current efficiency (A.C.E.) thus obtained has been compared with the cathodic current efficiency (C.C.E.) calculated by metal basis. A difference between the two values has been observed and the reasons for such differences have been analysed in this paper.

**KEY WORDS:** current efficiency, anode product, magnesium cells, chlorine gas analysis.

## INTRODUCTION

Energy consciousness in electrometallurgical industries has necessitated a fresh appraisal of the existing technologies, in order to update them for more clean and economical

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production of metals. Annual world output of Primary magnesium is about six lakh tonnes and nearly 80% is produced by the electrolytic process which is essentially decomposition of fused magnesium chloride into magnesium and chlorine and their subsequent discharge at the steel cathode and the graphite anode by the passage of a direct current. This being an energy intensive process, many improvements have been effected in both electrolyte chemistry and in electrolyser design by which the energy consumption has been brought down to 12 to 13 kWh kg<sup>-1</sup> in bipolar cells from 20 kWh kg<sup>-1</sup> in conventional cells. Further reduction in energy depends upon the improvement the C.E. which is the ratio of actual product collected to the theoretical quantity. It is the ratio of the metal recovered to the faradaic quantity and is an important parameter to assess the utility of the current and serves to understand the performance of any process. In metallurgical processes the C.E. is calculated from the metal output more so in electrowinning operations. Thus in magnesium electrolysis it is obtained by the relation,

$$\text{C.E.} = \frac{\text{metal produced (kg)}}{0.454 \times \text{current (kAh)}} \times 100 \dots\dots\dots(1)$$

Similar methods have been adopted to calculate the C.E. in various processes[1,2]. It is also possible to compute the C.E. from the anodic product because for the same quantity of current the extent of electrochemical reaction taking place must be same at the anode and at the cathode. The main aim of this study has been to calculate the C.E.

in magnesium electrolyzers from the volume of chlorine gas liberated at the anode. Free chlorine is determined by adding excess of antimony salt solution (relative to the chlorine concentration) and titrating the unreacted trivalent antimony amperometrically with KBrO<sub>3</sub> solution using platinum rotating electrodes[3]. Active chlorine concentration in a coloured solution is determined by adding antipyrine to bind definite amounts of chloride ion and then estimating the amount of reacting antipyrine using pyrimidone as the indicator[4,5] and in aqueous solutions by potentiometric methods[6]. Polarographic method for the determination of free chlorine in the presence of bonded chloride comprises the addition of an alkaline solution to a sample aliquot to set pH 9 to 10, heating the sample to complete decomposition of the bonded chloride and then determining the free chlorine[7]. A simple procedure has been proposed for the spectrometric determination of iodate by flow injection spectrophotometry and its modification was used for the determination of active chlorine and for automated routine determination of free chlorine in aqueous systems [8-10]. Chlorine in organic solvents can be easily determined by continuous automatic methods without interference by FeCl<sub>2</sub> or HCl[11]. An iodometric method has been used in this study to calculate the C.E. from the quantity of chlorine gas liberated during the electrolysis. The effect of current density and electrolyte composition on C.E. has been discussed. A comparison also has been made with the C.E. value obtained from the metal.

# EXPERIMENTAL

Experimental studies have been divided into two parts, namely a preliminary in which a series of electrolytic cells were operated with three different electrolytes : (a) NaCl 55, KCl 25,  $\text{MgCl}_2$  20% w/w , (b) NaCl 50, KCl 25  $\text{MgCl}_2$  25% w/w and (c) NaCl 50 , KCl 20 and  $\text{MgCl}_2$  30% w/w . The current density has been varied from 0.8 to 1.2  $\text{A cm}^{-2}$  in order to select the best electrolyte and the optimum current density at which maximum C.E. was obtained. The effect of current density and electrolyte composition on the C.E. calculated by (1) has been given in Fig.2. In the second part the selected electrolyte namely (a) and the optimum current density 1  $\text{A cm}^{-2}$  were used to operate a magnesium cell of size 620 X 370 X 420 mm, using bipolar electrodes made of graphite and steel at different capacities. In order to calculate the C.E., the total chlorine liberated at the anode as well as the chlorine concentration in the anode gas are required. To collect the required quantities, a simple experimental set-up has been used for measuring the total volume of chlorine-air mixture evolved from the cell and estimating the chlorine concentration in the mixture. This was done by drawing a known volume of chlorine-air mixture from the pipe line and absorbing the pure chlorine alone in concentrated alkali (40% w/w) after passing through a series of purifiers. An aliquot from the absorption vessel was treated with hydrochloric acid and KI and the liberated iodine was titrated against a standardised sodium

thiosulfate solution using starch as the indicator. Experimental set up used for the measurement of total volume, purification and absorption of the chlorine-air mixture is given in Fig.1.

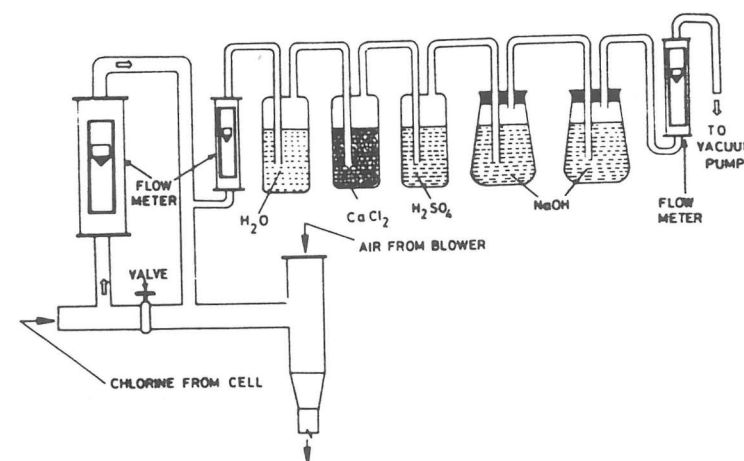


Fig:1 Set up for chlorine gas absorption

The total chlorine-air mixture from the cell was passed through a flow meter 250 l/min of rated capacity and the flow rate was measured. A known volume (10 l/min) was drawn from the same pipe and passed through a series of purifiers containing water, anhydrous calcium chloride and concentrated sulphuric acid successively to remove the contaminants. The purified stream was then passed through absorbers containing 40% w/w caustic solution maintained at a temperature of 278 K by using freezing mixture. The pure air coming out of the absorber was sent out after

measuring the flow rate by another flowmeter and ensuring complete absorption of chlorine tested by ammonia. In this study 500 ml of caustic solution in the first bottle and 300 ml of the same solution were taken in the second bottle. 60 l/min volume of chlorine-air mixture was passed for 30 minutes. The total quantity of chlorine in the absorbers was determined by iodometric and argentimetric methods, from which the C.E. was calculated using the relationship,

$$C.E = \frac{W \times V_t \times 75.75}{V_a \times KAh} \dots\dots\dots(2)$$

W -Total amount of chlorine in  $V_a$  in kg

$V_a$ -Volume of  $Cl_2$ /air absorbed for analysis in litres

$V_t$ -Total  $Cl_2$ /air evolving from the cell for 1 h in litres

Experiments were performed for different current capacities and durations. Both cathodic and anodic current efficiencies have been calculated using the relations (1) and (2) respectively.

#### RESULTS AND DISCUSSION

Cathodic current efficiencies calculated for the three electrolytes at different current densities are given in Fig.2 and a comparative data of current efficiencies are given in Table 1.

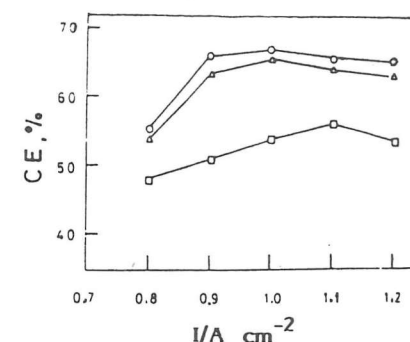


Fig.2 Plot of C.E. vs I for electrolytes

○- NaCl 55, KCl 25, MgCl₂ 20    △- NaCl 50, KCl 25, MgCl₂ 25  
and    □- NaCl 50, KCl 20, MgCl₂ 30

Table 1 : Comparison of anodic and cathodic current efficiency data

Electrolyte composition: NaCl 55, KCl 25 and MgCl₂ 20% w/w  
Current density: 1.0 A cm⁻²

Sl. No.	Current (kAh)	Mg metal (kg)	C.C.E. (%)	Chlorine (kg)	A.C.E. (%)	Relative error (%)
1.	1.0	0.26	57.20	0.80	60.35	-5.50
2.	1.0	0.28	61.60	0.82	61.86	-0.42
3.	2.5	0.80	70.40	2.30	69.41	1.40
4.	2.5	0.75	66.00	2.23	67.29	-1.95
5.	2.5	0.59	51.92	1.85	55.83	-7.53
6.	10.0	2.67	58.74	8.10	61.11	-4.03
7.	10.0	2.86	62.92	8.50	64.13	-1.92
8.	20.0	6.23	68.53	18.30	69.03	-0.73
9.	20.0	6.48	71.28	19.11	72.09	-1.10

### Effect of current density

It can be seen from Fig. 2 that the C.E. varies with the current density and the composition of the electrolyte. It is seen that the C.E. increases with increase in current density and the maximum C.E. is obtained at  $1.0 \text{ A cm}^{-2}$  for electrolytes 'a' and 'b' but for electrolyte 'c' the maximum C.E. is attained at  $1.1 \text{ A cm}^{-2}$ . This may be due to the prevalence of optimum current-voltage characteristics and minimum current loss at  $1 \text{ A cm}^{-2}$ .

### Effect of electrolyte composition

A four component system containing NaCl 35, KCl 35,  $\text{MgCl}_2$  20 and  $\text{BaCl}_2$  10% w/w has been tried in our institute for electrowinning of magnesium. Recently an effort has been made to eliminate  $\text{BaCl}_2$  and use a three component electrolyte. Among the systems, the one with NaCl 55, KCl 25 and  $\text{MgCl}_2$  20% w/w is found to be the most suitable since it gave the highest C.E. value. As the  $\text{MgCl}_2$  concentration decreases and NaCl composition increases the C.E. value increases. These may be due to the favourable conditions of optimum eutectic temperature, density, better coalescence, minimum metal solubility and higher conduction. On the basis of C.E. the electrolyte suitability can be graded as  $a > b > c$ . It can be seen from the table that the current efficiencies calculated from anodic and cathodic products are in the range of 50-70%. In most of the cases, A.C.E. is found to be higher than C.C.E. This may be due to the loss

of the metal in the sludge as well as by burning. In such situations the anodic product, chlorine gas is liberated without any loss. Similar explanations can be forwarded to substantiate the reduced cathodic current efficiency at lower current conditions. The observed behaviour can very well be explained by the enhanced metal output resulting from the following operational and physicochemical factors.

1. Metal collection is rather increased since a thick pool of molten metal is available due to higher impressed current.
2. At higher current, the discharge of chlorine and metal is comparatively higher, effecting higher circulation due to the enhanced hydrodynamic force where by the molten metal remains always buried within the molten electrolyte. In this way the metal is protected from burning which reduces the loss of metal.
3. At increased circulation and gas lift action the products are pushed apart quickly reducing the chance of recombination enhancing the value of C.E. The highest A.C.E. obtained was 72.09% as against C.C.E. of 71.3%. The lowest value of C.C.E. observed during the study was 52.0% and A.C.E. was 55.83% which were obtained while the cell was operating at low temperature resulting in solidification, shorting and spongy metal formation. It is evident from the above values that both current efficiencies are low due to the recombination of the metal and chlorine to form magnesium chloride.

The new approach of calculation of C.E. from anodic product paves way for explaining certain cell characteristics. It indicates the possible mechanism by which the metal has been lost. From the A.C.E. value one can also decide on the corrective action to be taken for a better performance of the electrolyser by incorporating necessary remedial measures. This study has further strengthened the observation that anodic current efficiency is always higher than C.C.E. in electrowinning operations particularly at high temperatures.

#### CONCLUSION

This study has provided another convenient method for calculating current efficiency in electrowinning operations particularly in magnesium electrolysis. The maximum value of current efficiency obtained by chlorine analysis was 72.09% which was found to be higher than the value computed by metal basis.

#### ACKNOWLEDGEMENT

The authors wish to thank their colleagues in electroprometallurgy division for full co-operation and Director, Central Electrochemical Research Institute for his permission to publish the paper. Constructive suggestions of the reviewers are also gratefully acknowledged.

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(Received, January 23, 1995  
Revised form, September 25, 1996)