Bulletin of Electrochemistry 16 (11) November 2000, pp 522-525 0256-1654/2000/$ 3-50

STUDIES ON THE ELECTROLYTIC DISSOLUTION OF SPHALERITE CONCENTRATE IN SULPHURIC ACID

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[Received: 23 May 2000 Accepted: 12 July 2000]

Efforts have been made to process a non conducting sulphide ore of zinc, namely Sphalerite, to electrowin Zinc from it, Sphalerite concentrate has been made conducting by mixing it with graphite powder and a concentration of 60% graphite has been chosen as the optimum concentration. Anodic dissolution of Sphalerite concentrate obtaining from Hindustan Zinc Ltd.. Udaipur, India in H_2SO_4 solution has been investigated using statistical design of experiments. It is found that maximum efficiency has been obtained when anodic current density and acid concentration are low and the temperature is above the room temperature.

Keywords: Zinc sulphide, electrolytic dissolution, electrowinning and statistical design.

INTRODUCTION

Major mineral sources for base metals like Copper, Zinc, Lead, Nickel and Cobalt and found to occur as sulphides which are good semi conductors. Conventionally these minerals have been processed either wholly by pyrometallurgical routes or by a combination of pyro and hydro metallurgical methods. Most of the sulphides except Sphalerite are very good conductors of electric current. Hence efforts were made as early as in 1882 to make use of cast copper-lead matte as anodes in electrolytic cells [1] Nickel sulphide matte which essentially is pure Ni_3S_2 forms the anode of the electrolytic cell in the process used by International Nickel Company, Canada [2] and Sumitomo metal refinery, Japan [3]. The anodic process is essentially the oxidation of sulphide to elemental sulphur. Similar investigations have been carried out using copper matte, copper sulphide [4-7] and galena [8-9]. Efforts have also been made to electrowin Zinc from Sphalerite directly [10]. In the present study the anodic dissolution of Sphalerite concentrate in sulphuric acid has been investigated using statistical design of experiments.

EXPERIMENTAL

Sphalerite concentrate used for electrolysis is procured from M/s Hindustan Zinc Ltd, Udaipur, India. The partial chemical analysis of Sphalerite concentrate is given in the Table I AR grade H_2SO_4 has been used. Solution of required concentration was prepared using distilled water.

The electrolysis was carried out in a glass beaker of 1 litre capacity. 500 ml of sulphuric acid of required concentration was taken in the beaker. The anode consists of Sphalerite concentrate mixed with graphite powder and

TABLE I: Partial chemical analysis of Sphalerite concentrate

Element	Percentage (%)
Zn	50.50
S	31.61
SiO_2	4.60
Fe	8.08
Pb	1.74
Cd	0.81
Cu	0.28
MgO	0.58
CaO	0.55

packed in a PVC cylindrical container of 10 cm length and 3.8 cm diameter having small holes all around. A polypropylene cloth bag is would around the vessel to avoid the entry of solid particles through holes into the electrolyte. A graphite rod acts as the current lead. The design of the anode is shown in Fig. 1. Sphalerite was mixed with different amounts of graphite powder thoroughly and packed in the PVC container after keeping the graphite rod at the center of the vessel. The vessel is then closed with a light fitting lid. The vessel is then allowed to soak in the electrolyte for one hour before starting the experiment. The cathode is an aluminium sheet of dimension 3 cm x 5 cm. A water thermostat was used to maintain the cell temperature at a constant value. The potentials of different composition are noted for different currents to fix up an optimum concentration of packed bed. At the end of each experiment the packed bed is washed well by keeping the packed bed in a beaker containing water, the wash water is added to the original electrolyte and the zinc content in the electrolyte is estimated volumetrically using EDTA [11]

Factorial design

A free factorial of the type p^x [12-15] is used in the present study. Here k denotes the number of factors. Each factor is varied at p numbers of levels. The variables chosen for the present study are anodic current density (X_1), temperature (X_2) and acid concentration (X_3). These variables are varied simultaneously at two levels namely the upper level (+1) or the lower level (-1). i.e P = 2. Eight trials were required for an experiment with three factors varied at low levels. In addition to this three more experiments have been carried out at the base level (zero level) to estimate the error variable and to test the significance of coefficients and the adequacy of the model obtained. The actual and coded values of variable are given in the Table II. 2^3 factorial design of the anodic dissolution is shown in Fig. 2 if the response variables current efficiency is represented by Y, then for the present experiment the regression equation relation Y and other coefficients are usually represented as

TABLE II: Actual and coded values of variables

Level	X_1 c.d. $A.m^{-2}$	x_1 coded value	X_2 Temp K	x_2 coded value	X_3 acid conc $g.dm^{-3}$	x_3 coded value
Upper	600	+1	333	+1	200	+1
Base	400	0	318	0	125	0
Lower	200	-1	303	-1	50	-1

$$Y' = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \quad (1)$$

$$\text{Here } b_0 = \frac{\sum_{1}^{8} Y_i}{N} \quad (2)$$

$$\text{and } b_j = \frac{\sum_{1}^{8} X_{ji} Y_i}{N} \quad (3)$$

b_0 represents the average anodic current efficiency for 8 trials (excluding the base level experiments) b_1, b_2 and

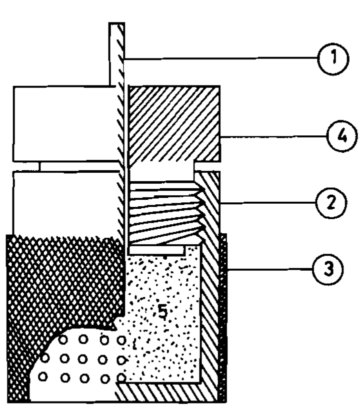

Fig. 1: Sectional view of the packed bed electrode
(1) Graphite rod (2) PVC cylindrical vessel
(3) Diphragm cloth (4) Threaded lid
(5) Packed bed of ZnS conc. and graphite

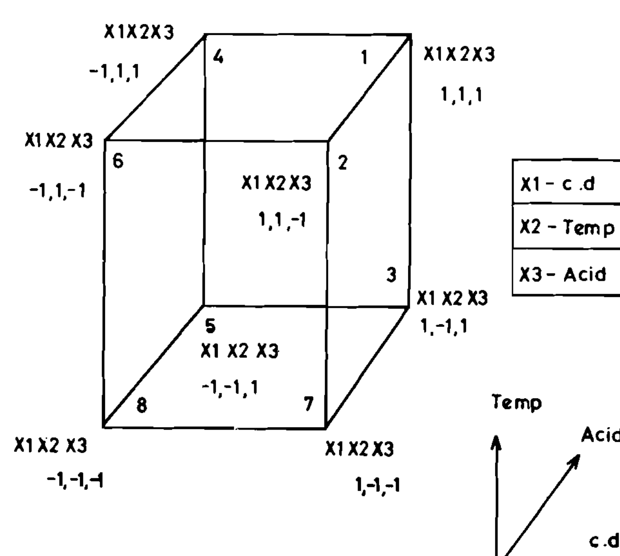

Fig. 2: 2^3 Factorial representation of Zn dissolution from Sphalerite

TABLE III: Vibration of the electrode potential with graphite content in the packed bed

Current mA	Electrode potential V vs SCE (Graphite content in the bed) 20	30	40	50	60
0	0.285	0.380	0.360	0.370	0.370
100	1.710	1.260	0.730	0.570	0.510
200	2.660	2.110	1.040	0.800	0.620
300	3.570	2.770	1.380	1.020	0.810
400	4.180	3.190	1.710	1.250	1.090
600	5.530	4.000	2.410	1.750	1.450
800	6.700	4.700	3.310	2.400	1.830
1000	8.040	5.400	3.930	2.970	2.210

b_3 are coefficients representing the effect of each factor namely current density temperature and concentration. b_{12}, b_{13}, b_{23} and b_{123} are regression interaction coefficient of concerned variables. The relation between the actual and coded values are:

$$X_1 = \frac{X_1 - 400}{200}$$

$$X_2 = \frac{X_2 - 318}{15}$$

$$\text{and } X_3 = \frac{X_3 - 125}{75} \quad (4)$$

RESULTS AND DISCUSSION

Table III shows the variation of electrode potential with current for different graphite content. It can be seen that electrode potential decreases with increase in graphite content in the bed. Packed bed containing graphite more than 60% of sphalerite in the bed has not been tried in the present study because of the fact that it will reduce the quantity of electroactive material. So all the experiments in this study have been carried out in a packed bed containing synthetic graphite powder to the extent of 60%. The bed contains 25 g of Sphalerite concentrate and 15 g of graphite powder.

Table IV gives the complete design matrix based on the coded scale. It also gives the current efficiency for the dissolution of Sphalerite under different experimental conditions. After inserting the values of coefficients in the equation (1) the regression equation becomes

$$Y' = 27.64 - 16.27x_1 + 12.14x_2 - 5.32x_3 - 8.04\, x_1x_2 - 4.12\, x_2x_3 + 1.54\, x_1x_3 + 3.49\, x_{x_2}x_3 \quad (5)$$

The test of the significance is carried out for each coefficient of the regression equation using students 't' test at 5% level ($\alpha = 0.05$) of significant. It is found that b_{13} is insignificant. Fischer's adequacy test indicates that the model is adequate at 95% confidence level as the calculated F ratio does not exceed the tabulated one. Then the predicted value of current efficiency for zinc dissolution Y is given by:

$$\hat{Y} = 27.64 + 16.27\, x_1 + 12.14\, x_2 - 5.32\, x_3 - 8.04\, x_1x_2 - 4.1\, x_2x_3 + 3.49\, x_1x_2x_3 \quad (6)$$

It can be seen from equation (6) that current density exerts maximum influences on the dissolution of

TABLE IV: Design matrix for the anode dissolution of Sphalerite concentrate in packed bed

X_0	X_1	X_2	X_3	X_1X_2	X_2X_3	X_1X_3	$X_1X_2X_3$	C.E. (%)
+1	+1	+1	+1	+1	+1	+1	+1	11.06
+1	+1	+1	-1	+1	-1	-1	-1	19.88
+1	+1	-1	+1	-1	-1	+1	-1	4.12
+1	-1	+1	+1	-1	+1	-1	-1	49.61
+1	-1	-1	+1	+1	-1	-1	+1	24.49
+1	-1	+1	-1	-1	-1	+1	+1	78.57
+1	+1	-1	-1	-1	+1	-1	+1	10.42
+1	-1	-1	-1	+1	+1	+1	-1	23.00
—	0	0	0	—	—	—	—	23.57
—	0	0	0	—	—	—	—	23.27
—	0	0	0	—	—	—	—	22.97

TABLE V: Parameters chosen for the verification of regression equation and the current efficiency obtained

Parameters						Anodic current efficiency (%)	
Anodic current density $A.m^{-2}$		Temperature K		Acid concentration			
Actual	Coded	Actual	Coded	Actual	Coded	Experimental	Regression equation
500	+0.833	323	+0.833	75	-0.66	24.50	22.85

Sphalerite. Its effect is negative, there by indicating a fall in current efficiency with increase in the current density. This is in agreement with observation by other workers [10,16] in the case of zinc sulphide. Similar effects have been reported in the case of Cu_2S (6) and PbS [17]. The temperature is found to play an important role in electrochemical reactions. Mostly it has a beneficial influence on current efficiency. The regression equation shows the positive role played by temperature. The beneficial influence of temperature on current efficiency has already been reported by several authors [6,16-17].

The regression equation shows that the acid concentration has a negative influence. Similar observation has been made [6] but current density has a more predominant influence than the acid concentration.

Verification of the model

To verify the regression equation obtained, a trial run has been made choosing the parameters within the range of chosen parameters. Table V gives the values of experimental and theoretical values (obtained using the regression equation) of parameters and current efficiency. Both the values differ by only 1.65% which is within the limit and thus proves the usefulness of the model.

CONCLUSION

The statistical design of experiments in the study of anodic dissolution of Sphalerite concentrate shows that maximum current efficiency can be obtained when anodic current densities and acid concentration are low and the temperature is above the room temperature.

Acknowledgment: Authors are thankful to Sri K Venkateswaran, Head, Electrometallurgy Division for his keen interest in this work. They also thank the Director, Central Electrochemical Research Institute, Karaikudi, Tamil Nadu for his kind permission to publish this paper.

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