JOURNAL OF APPLIED ELECTROCHEMISTRY 7 (1977) 175–179

Continuous electrolytic reduction of a chalcopyrite slurry

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Received 13 September 1976

A laboratory-scale cell for the continuous electrolytic reduction of chalcopyrite contained in copper concentrate is described. Dry concentrate is fed into one end of the cell and forms a particulate bed electrode, with fluidized properties, resting on the copper cathode constituting the cell base. At the opposite end, the reduced product containing copper sulphide of composition $Cu_{1.8}S$ to Cu_2S flows over a weir. The feed rate determines the coulombic efficiency and extent of reduction of the sulphide. A copper extraction process incorporating slurry electrolysis is proposed and scale-up problems discussed

1. Introduction

Recent work [1] has shown that the copper mineral chalcopyrite ($CuFeS_2$) can be electrolytically reduced in a slurry or particle bed contacting a metal cathode. The main reaction is of the form

$$2CuFeS_2 + 6H^+ + 2e \rightarrow Cu_2S + 3H_2S + 2Fe^{2+} \quad (1)$$

giving an iron-free copper sulphide product whose composition can be in the range $Cu_{1.8}S$ to Cu_2S [1, 2]. This type of reaction is potentially of interest for hydrometallurgical copper extraction processing, since it gives an early separation of copper and iron and yields a product from which copper is leached more readily than from the rather inert chalcopyrite. A major problem is that a significant fraction of the current is consumed in the hydrogen evolution reaction. As an extension of the earlier work [1], which was mainly concerned with optimizing the current efficiency in batch electrolysis, we have examined the possibility of carrying out slurry reduction in a continuous manner. This paper describes a cell design, reports on its performance, and suggests a copper extraction process incorporating the slurry electrolysis of chalcopyrite.

2. Experimental

The design of the continuous cell was based on the principles applied earlier [1] in slurry electrolysis under batch conditions – horizontal disposition of the electrodes, use of a diaphragm, increase of the ratio of electrolyte volume to cathode area by using a trough-shaped cell, and operation at high current densities which had the effect of fluidizing the slurry. A general view of the cell and a vertical section are shown in Fig. 1.

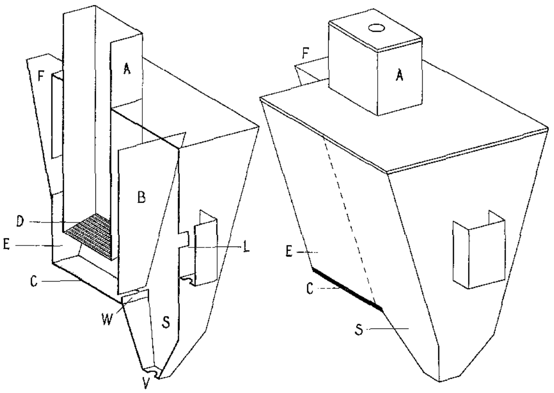

Fig. 1. Schematic view and vertical section of slurry electrolysis cell. A, anode compartment; B, baffle; C, cathode; D, diaphragm; E, electrolysis compartment; F, feed chute; L, electrolyte overflow; S, settling compartment; V, valve for product withdrawal; W, weir.

The construction material was Perspex. The body of the cell was divided into two compartments by a baffle, B. Electrolysis was carried out in compartment E, the base of which consisted of a copper cathode, C (9 × 4 cm). The anode was in a separate compartment, A, a PVC tube of rectangular section mounted in the cell lid so that it was suspended above the cathode. The diaphragm, D, was fabricated as before [1] from polyester filter cloth and shaped to avoid trapping of gas. The anode (not shown) was platinized titanium expanded mesh welded onto titanium rod.

Circulation of electrolyte was not in itself a requirement for the proper operation of the cell. However, compartment E did not contain sufficient catholyte to allow completion of an experiment without severe depletion of the acid concentration. Hence, electrolyte was pumped from an external reservoir (3 l), entering the cell through the concentrate feed chute F and leaving the overflow L which maintained a constant electrolyte level. Provision was made in both the reservoir and the electrolyte circuit for controlling the electrolyte temperature.

Dried, screened copper concentrate was fed into the chute F by a small screw feeder. The level of the particle bed was controlled by the weir W over which the product passed into the settling compartment, S. From here, the product could be drawn off through a valve, V. Both the weir and the baffle were fitted in slots in the cell wall to allow removal and alteration of their dimensions.

Experiments were conducted by loading 20 g of slurried concentrate into the electrolysis compartment and starting the feeder, electrolyte pump, and current simultaneously. The copper concentrate used, from The Mount Lyell Mining & Railway Company Limited, Tasmania, contained 25·2% Cu, 29·4% Fe, and 34·8% S. Most experiments were carried out at a current of 30 A (8300 A m^{-2}) with an electrolyte of 4 M HCl, and the total charge passed was 10^5 C. Coulombic efficiency on the basis of Reaction 1 was assessed as before [1] by analysis of the electrolyte for dissolved iron and defining coulombic efficiency as mol Fe^{2+} F^{-1}. Correction was made for a contribution due to acid-soluble iron (i.e. with no current) which became significant with the large quantities of concentrate (up to 0·7 kg) passing through the cell. The correction amounted to 0·9 g Fe for each 100 g concentrate reacted.

3. Results

The criterion for successful physical operation of the cell was that the rate at which reacted material passed over the weir into the settling compartment should be determined by the rate at which concentrate was fed to the cell. This behaviour implied a steady-state condition of the particle bed electrode and seemed to depend on fluidization of the slurry by the vigorous gas evolution at high current densities. Two factors were found to be important. If the bottom of the baffle was below the weir level, slurry flow was impeded and the bed built up gradually. With the baffle above the weir (a gap of 0·2 cm was generally used), the cell operated well, over a range of weir heights from 0·2–1·3 cm. The other factor affecting smooth operation was the concentrate feed rate. At low feed rates there was an increased tendency for reduction to proceed beyond Reaction 1, according to

$$Cu_2S + 2H^+ + 2e \rightarrow 2Cu + H_2S. \qquad (2)$$

The copper formed in clumps, binding particles of reacted concentrate together and inhibiting free flow of the slurry. In such cases a short period of agitation with a glass rod restored slurry flow.

At a given temperature and acid concentration, feed rate was the critical operating parameter that determined the fraction of chalcopyrite being reduced and the coulombic efficiency for the process. Typical results for operation at 70° C are shown in Fig. 2 and Table 1. Earlier work [1] indicated that a higher temperature would have given improved coulombic efficiencies, but there was doubt that the Perspex cell could withstand temperatures in excess of 70° C.

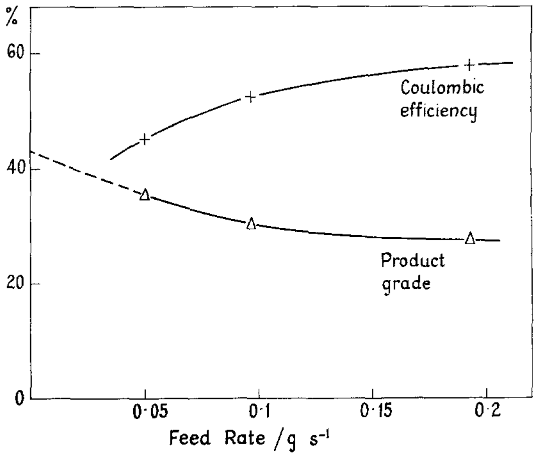

Fig. 2. Coulombic efficiency for chalcopyrite reduction, and copper grade of product, as functions of feed rate. 4 mol dm^{-3} HCl, 70° C.

Table 1. Experimental and calculated values of product copper grades for data of Fig. 2. (Feed grade 25·2% copper)

Feed rate	*Coulombic efficiency*	*Product grade* (% Cu)	
($g\,s^{-1}$)	(%)	*Calc.*	*Obs.*
0·050	45·1	35·6	35·4
0·097	52·3	30·5	30·2
0·193	57·7	27·9	27·5

In order to simulate a two-stage process, the product from a run at a feed rate of 0·192 $g\,s^{-1}$ (coulombic efficiency 63%) was dried and used as a feed material in a second run under similar conditions. Electrolysis proceeded satisfactorily, with a coulombic efficiency of 42%.

One possible route in processing a copper concentrate (see below) involves further electrolysis of a leach residue. This was tested as follows. The product from a run at 0·193 $g\,s^{-1}$ (coulombic efficiency 59%) was leached for 2 h at 80° C in a solution containing 0·7 mol dm^{-3} $CuCl_2$, 3·5 mol dm^{-3} NaCl, and 1·0 mol dm^{-3} HCl, according to the method developed by Cathro [3]. This procedure gives selective dissolution of copper from copper sulphides, which are more rapidly oxidized than chalcopyrite. Elemental sulphur was extracted with carbon disulphide and the dried residue passed again through the electrolysis cell at a feed rate of 0·117 $g\,s^{-1}$. Operation was normal, and the coulombic efficiency was 44%.

4. Discussion

4.1. *Coulombic efficiency*

The experimental work described above demonstrates the feasibility of carrying out the electrolytic reduction of a chalcopyrite slurry in a continuous manner. During its passage across the cell each particle of concentrate leaves and returns many times to the particle bed electrode, as a consequence of the vigorous agitation by hydrogen sulphide and hydrogen evolved in the cathode reactions. Reduction is by a direct electrolytic mechanism [1], and the extent of reduction of a given particle is determined by its residence time in the cell. The general movement of particles across the cell towards the weir is ensured by the fluidized state of the slurry and the response to the entry of concentrate at the opposite end of the cell.

The influence of feed rate on coulombic efficiency for chalcopyrite reduction is consistent with previous results from batch experiments [1]. There it was shown that the instantaneous current efficiency falls progressively with extent of electrolysis, due to the influence of a thickening layer of copper sulphide product on the rate of diffusion of ferrous ion away from the reaction zone [1, 2]. In the same way, the current efficiency in the continuous mode of operation falls with increasing residence time, because of the increased product thickness on each particle. This is reflected in the influence of feed rate on coulombic efficiency shown in Fig. 2. Similarly, in the simulated two-stage process, the second electrolysis step has a lower efficiency because the particles enter the cell with a layer of product already on their surfaces.

With the leach residue, the coulombic efficiency was 44% compared with 54% expected from the curve in Fig. 2 for the feed rate used. Here, the chalcopyrite particles are probably clean but are more diluted by pyrite and gangue than in the original concentrate. Although the relative contributions of pyrite particles, reduction products, and metal cathode in evolving hydrogen are not fully understood [1], it seems clear that this dilution of the chalcopyrite content leads to the loss in coulombic efficiency observed.

The limited data of Fig. 2 suggest that the coulombic efficiency at high feed rates approaches an upper limit of around 60%. This is consistent with the initial current efficiency of 60% found previously [1] for batch electrolysis under similar conditions.

4.2. *Product grade*

The practical aims of the electrolytic reduction are to convert copper in the concentrate into a more reactive form and to produce a material which is upgraded in respect to its copper content. Although a higher feed rate gives a greater coulombic efficiency, the proportion of chalcopyrite which is reduced in passing through the cell is smaller. In the limit, the copper grade of the product would equal that of the feed. At the other extreme, with the feed rate approaching zero, the limit of product grade, when all chalcopyrite is reduced, is calculated from Equation 1 to be 42·9%. The broken curve in Fig. 2 shows that the experimental data can be extrapolated smoothly to this value at zero feed rate.

For intermediate feed rates, the theoretical product grade can be calculated from the current (I, A), feed rate (R, g s^{-1}), and experimental coulombic efficiency ($C.E.$) as follows. From Equation 1 the loss in weight in forming copper sulphide from chalcopyrite is $C.E. \times 103{\cdot}9$ g F^{-1}. The weight loss is therefore ($C.E. \times 103{\cdot}9\, I/F$)g s^{-1}. and the product grade for steady-state operation of the cell is given by the relation

$$\text{Product grade} = \text{Feed grade} \times \frac{R}{R-(C.E. \times 103{\cdot}9\, I/F)}. \qquad (3)$$

There is a good agreement between the calculated and observed product grades given in Table 1.

4.3. *Process considerations*

Some of the many possible options for incorporating an electrolytic procedure of the kind described into a hydrometallurgical copper extraction process were discussed previously [1]. The example shown in Fig. 3 is chosen for further consideration since most of the steps have been shown to be feasible, the cupric chloride leaching route is attractive because of its ability to give a leach liquor low in iron, and the products, shown at the right of the diagram, are all in a desirable form. No attempt will be made here to make an economic assessment of the process, or a comparative evaluation of potentially competing processes such as the many hydrometallurgical routes for copper that have emerged in recent years in response to air pollution legislation (e.g. [4]).

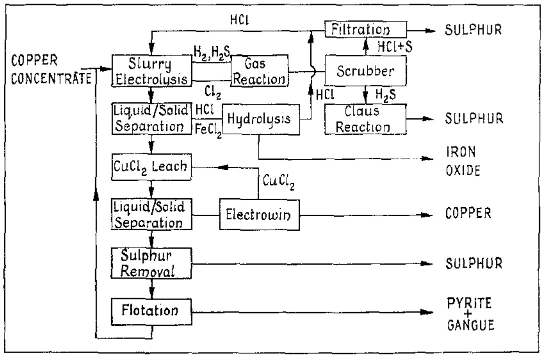

Fig. 3. Simplified flowsheet for copper extraction process incorporating slurry reduction of chalcopyrite.

The flowsheet starts with slurry electrolysis. The reduced solid product is leached and copper recovered from the leach solution [3]. The leach residue contains chalcopyrite, pyrite, gangue and sulphur. The latter is extracted with a suitable solvent, and chalcopyrite is separated from the other solids by flotation and returned for slurry reduction. Alternatively, another slurry electrolysis step (not shown) could be carried out after sulphur removal, as was shown to be feasible in the experimental work described above.

The other main branches of the flowsheet involve (a) reaction of the gases produced by electrolysis to form hydrogen chloride and sulphur, with excess hydrogen sulphide bring treated in a Claus kiln to recover sulphur, and (b) treatment of electrolyte by one of a number of available oxidation–hydrolysis processes (e.g. [5]) for regeneration of hydrochloric acid and production of iron oxide.

Since this paper is mainly concerned with slurry electrolysis, some comments on cell design, operation, and scale-up are pertinent. Residence time is an important parameter in view of the results discussed above. Because of the influence of feed rate on coulombic efficiency, the most economic use of electrical power is at a high feed rate, but this must be weighed against the penalty of an increased circulating load of unreacted chalcopyrite. It is also important to recognize that the type of horizontally disposed cell used here cannot effectively be scaled-up in the vertical direction. A thicker particle bed would not allow a higher current density to be used and, in addition, experience indicates that a bed of concentrate thicker than 1.5–2 cm loses the desirable fluidized properties on which continuous operation depends. Scale-up in horizontal dimensions may also introduce problems since, for a given residence time the actual speed of movement slurry across the cell must increase with cell length. Some form of mechanical agitation or raking may be necessary in cells of a practical scale.

Any consideration of scale-up prompts the question as to whether a cell with vertical electrodes would be preferable to the type used here. This would effectively allow scale-up in three dimensions, with consequent savings in plant area. The closest analogy to the the present arrangement, with a particle bed lying on a cathode, would be a vertical cell employing a thick slurry pumped through the cathode compartment. Such a unit, if operated at the present current densities, would have to overcome the problems caused by the evolution and escape of large volumes of gas from a deep, narrow cell. Vertical cells would place heavy demands on the diaphragm which must minimize exchange between anolyte and catholyte yet have a low electrical resistance and be able to withstand both abrasion by the slurry and attack by chlorine at elevated temperatures. Despite these difficulties, advancing technology in fluidized bed and slurry electrodes (e.g. [6]) may well make a vertical cell practical for chalcopyrite reduction.

References

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