FLUIDIZED BED ELECTRODE; A NOVEL TECHNIQUE IN EXTRACTIVE METALLURGY

S. C. Das

Regional Research Laboratory, Bhubaneswar-751013.

(Received June 1978; accepted July 1978)

The fluidized bed reactors are well known in chemical technology. But the concept of fluidized bed in electrochemical technology is a recent one. In the following article the concept of fluidized bed electrode system, including electrode configeration, types of bed used and its advantage over stationary electrodes are discussed. The probable use of fluidized bed electrode in extractive metallurgy is thoroughly reviewed.

In the application of electrochemical processes one of the main difficulties is scaling up. In electrochemical process the surfaces at which reaction takes place are electrodes and the capacity of the equipment used is determined by the electrode area available. Much less scale-up advantage is available in electrochemical processes because of the dependance of capacity on electrode area and the need to locate accurately these electrodes in the equipment. One major element of modern thinking in electrochemistry is the "small volume-high current" principle. One recent invention for increasing electrode surface area per unit volume of plant, which is hoped to produce increased through-put, has been the concept of a fluidized bed electrode. Fluidized bed reactors are are well known in chemical technology and are specially suited for catalytic reactions with internal-pore diffusion control; the fluidized catalyst has a much larger effective surface area than its fixed bed counterparts.

In a fluidized bed electrode system, the electrode consist of a bed of solids, electrically conducting particles supported on a sintered or porous base through which an electrolyte can be pumped. The flowing electrolyte causes the bed to expand so that the electrolyte flows smoothly between the particles. Electrical contacts to the bed is made by an inert conducting wire, plate or mesh which may be called feeder and which is inserted into the bed. In a fluidized bed electrochemical reactor the effective current conducting area is sufficiently larger to allow the flow of large electric currents in a relatively small reactor volume, without effecting unduely large current densities.

The idea of fluidized bed electrode for the first time was reported by Goodridge[1] together with Backhurst and fleishman[2,3] during late sixtees. Actually the idea stemmed from the observation that when a bed of conducting particles is fluidized by an upward flow of electrilyte the bed can function as an electrode. Such a particulate electrode offered a considerable increase in electrode surface area over a conventional plate electrode occupying the same volume, and the surface area could be varied by varying the particle size.

THEORY AVAILABLE ON FLUIDIZED BED ELECTRODE :

Not much work on the mathematical analysis of fluidized bed electrode has been carried out. Goodridge and Coworkers[4,5] have developed a mathematical model which is based on the description of a current flow through the dispersed phase and the electrolyte phase in terms of the "charge transfer" coefficient, K_m for the particulate phase and the "effective specific conductence", K_s for the electrolyte phase. Therefore the current flowing in two phases may be expressed as :

$$\text{dispersed phase : } I_m = -K_m A \frac{d\Phi_m}{dx}$$

and

$$\text{electrolyte phase : } I_s = -K_s A \frac{d\Phi_s}{dx}$$

The total current I_L is given by $I_L = I_m + I_s$ Where: A = Cross Section area of the bed in the direction of current flow; I_m = Current supported by particulate phase; I_s = Current supported by electrolyte phase; K_m = Charge transfer coefficient for the particulate phase; K_s = Charge transfer coefficient for the electrolyte phase; Φ_m = Particulate phase potential; Φ_s = Electrolyte phase potential; and x = Distance from feeder in the direction of current flow.

The differential equations were solved via analogue computer for a concentric cylindrical electrode ($d\Phi_m/dx = 0$ at the bed houndary and $d\Phi_s/dx = 0$ at the feeder surface). The theory predicted for the fludized bed electrode by Goodridge and Coworkers[4,5] compares reasonably well with the experimental observation[3] concerning potential distributions. The concept of charge transfer via intermittent particular

contact proved especially useful in interpreting the non uniform behaviour of the fluidized bed electrodes in the neighbourhood of the flow distributor.

This behaviour can apparently be explained by the local variation of the charge transfer coefficient while non-uniform flow around the distributor is most probably a hydrodynamic phenomenon. The values of K_m obtained in a given electrical configuration can probably be used in other configuration so long as the hydrodynamic conditions are essentially identical

TYPES OF ELECTRODE CONFIGURATION:

Mainly two types of electrode configurations are considered, i) Plane parallel and ii) Side by side configuration.

i) Plane parallel configuration :

In this type of electrode configuration, electrolyte is passed through a porous support on which the bed rests and passes out of the cell at the top. The current feeder is located in the bed and is perpendicular to the direction of electrolyte flow. The other electrode is is usually a grid, located just above the expanded bed. Here, in such a configuration there are no separate anolyte and catholyte streams and the flow of current is parallel to the electrolyte flow.

ii) Side by side configuration :

Here the cell is divided into an anode and cathode compartments by a membrane which serves both as a separator for the anolyte and catholyte and a support to the bed. The current feeder is usually either a metal mesh or a series of parallel metal rods inserted into the bed, In this configuration the current flow is perpendicular to the electrolyte flow and either or both electrodes can be fluidized.

Scale-up of these beds can take place in a direction parallel to or at right angles to the direction of current flow. The scale-up of bed height at right angles to the flow of current yields a linear relationship of bed current to height. But scale-up in the direction parallel to the current flow is very limited because this is governed by the position of the current feeder and the potential distribution in the bed. Increasing the thickness of the bed beyond a certain point, will yield no useful increase in the current and a fraction of the available surface area of beds of thickness greater than this limiting value will be completely inactive.

TYPE OF ELECTRODE BED

The fluidized beds can be divided into the types depending on the types of bed of particles. i) insulating particles and ii) conducting particles.

i) Fluidized bed of insulating particles :

The insulating particles used for the purpose of beds is invariably glass beads. The presence of fluidized bed of insulating particles has two effects which act in opposite directions : i) the mean conductivity of the electrode space decreases, since the volume fraction filled by the conducting liquid decreases. 2) the concentration overvoltage η remains negligible even for the strongest current densities used.

ii) Fluidized bed of conducting particle.

The presence of a fluidized bed of non-conducting grains has the drawback of reducing the conductance of cell by about 50%. This disadvantage can be avoided by fluidized grains of conducting material. For example in copper sulphate solution electrolysis when glass beads are substituted by copper beads of the same diameter the apparent conductance of the cell increases. But care must be taken to see that the conducting material should not interfere with the electrochemical reactions taking place in the cell.

Advantages of Fluidized Bed Electrodes.

The fluidized bed electrodes appear to present many advantages and may be summarized as follows :

i) The contact area of the electrode is very large (100 to 1000 cm^2 cm^3); ii) The fluxes of mass and heat transfer between fluid and electrode are very large; iii) the electrode can be regenerated in continuous manner; iv) The system is very versatile and allows control by many variables.

In a large continuous cell, the fluidized bed will act as a stirrer and will increase the homogeneity of the electrolyte, and concentration gradient will be reduced. If concentration polarisation is a restrictive phenomenon, the fluidized bed allows a considerable increase in the current density. In a sence it constitutes a means of control of the diffusional process that allows the industrial scale-up of a process.

Fluidized Bed Electrode Technique Applied to Extractive Metallurgy:

In extractive metallurgy electrolytic processes like electrowinning and electrorefining play a major role. Considering the special advantages of the fluidized bed systems, it has been realised to apply this to extractive metallurgy. Use of a fluidized bed electrode may be advantageous in electrowinning to gain an increased through-put by the large increase in total cell current while keeping the current the same. Similarly direct electrorefining of impure particulate metals such as cement copper may be possible. Cases where dump leaching is carried out to extract the metal, usually increasing volume of dilute leach liquors are obtained. In these cases it is really impossible to use it for direct electrolysis. At present such liquors are treated by techniques such as cementation, solvent extraction or ion exchange, but never by direct electrolysis because of the concentration polarisation which makes the system uneconomic. But it is possible to use a fluidized bed electrode which provide cell currents, comparable with existing plate systems, with much reduced current density per unit surface area. The reduced current density per unit surface area prevents rapid depletion of the Nearest layer on the cathode which causes the onset of polarisation.

The application of fluidized bed electrodes for the extraction of metals is very recent one. Uptil now a very few systems have been tried with fluidized bed i.e., extraction of nickel, zinc and copper from very dilute solutions.

Vergnes[6] has described a nickel electroplating apparatus using electrically inert grains as the fluidizing medium. The surface quality of the plated metal coat was comparable with that obtained via conventional plating cells and the cell carried limiting currents up to five times the conventional quantity.

Plimley and his colleagues[2] tried to deposit zinc on a fluidized bed electrode. They used copper coated glass spheres (particle size 452-520μ) as the beds and the electrolyte composed of 2 M KOH and 0.1M $ZnSO_4$ solution. A nickel disc formed the counter electrode and the bed was supported on a glass sinter. In a typical run the bed consisted of 10g. of copper coated glass spheres, fluidized to an expansion of 50% and a current of 1.6 A was passed for a period of 3 hr. at room temperature. It has been seen that in this run a current efficiency of 85% has been obtained.

As compared with nickel and zinc a more detailed study has been carried out on copper recovery from dilute solutions. Thangappan et al[7] carried out a series of experiments for the deposition of copper, using close cut silica sand and glass beads as fluidizing agents and compared the results with that of stationary electrodes in the same apparatus using i) a stagnent electrolyte and ii) a flowing electrolyte. Fluidized electro-forming resulted in surfaces of better quality and according to authors, this was due to improved current distribution along the cathode and the removal of H_2 bubbles clinging to it. Table - 1 shows the principal properties of the set-up and the observed limiting current density.

TABLE - 1 The principal properties of a copper electroforming process in an inert fluidized bed.

Bath composition: (A) $CuSO_4.5H_2O = 150 \pm 2 gdm^{-3}$; $H_2SO_4 = 50 \pm 1 gdm^{-3}$
(B) $CuSO_4.5H_2O = 250 \pm 2 gdm^{-3}$; $H_2SO_4 = 100 \pm 1 gdm^{-3}$

	Glass Beads	Silica Sand
Average particle diameter, Cm	0.050	0.0592
Specific gravity of particle	2.23	2.64
Minimum fluidization velocity, CmS^{-1}: Bath A	0.120	0.145
Bath B	0.098	0.118

Effective Cell Volume = 0.136 dm^3
Maximum current intensity = 588 A dm^{-2}

	Limiting Current i_L Adm^{-2}	
	Bath A	Bath B
Stationary Electrode, Stagnant Electrolyte	11.0	16 0
Stationary Electrode, Flowing Electrolyte		
Flowing Electrolyte $\rho = 2.43$ Cm S^{-1}	29.0	42.0
Fluidized Bed Cell $\rho = 2.43$ Cm S^{-1}	65.0	80.0

Surfleet[8], using a fluidized bed of plane parallel configuration showed that the rate of deposition of

copper is increased by reducing the p^H of the electrolyte (2g l $CuSO_4$) and that the current efficiency is independent of p^H. The fluidized bed cathode has got advantage over a plate cathode when composed under similar conditions. On the basis of the results obtained he has proposed a flow sheet. The flow sheet was a simple one in which the particles charged initially were fluidized by copper-containing electrolyte and then they were removed when they had grown sufficiently large. Seiving of the particles was suggested, with the oversize being passed to melting and the undersize being returned to the cell. The detailed studies of Fleet[9–11] on copper electrowinning on fluidized bed electrode is a valuable contribution to fluidized bed technique. For the priliminary study he used a cell made of a cylinder of 33 mm radious with porous glass on which the fluidized bed rests.

TABLE – 2 Comparison data for fluidized cathode, plate cathode and conventional electrowinning system.

System	Time of electrolysis (min)	Cell Current (A/m^2)	Copper removed (%)	Current efficiency (%)	Power efficiency (KgCu/Kwh)
Fluid bed cathode	65	194	83	80	0.566
Fluid bed Cathode	30	442	98.7	99.7	0.454
Fluid bed 2	15	787	92.0	92.0	0.381
Plate Cathode	60	108	26.2	49.2	0.027
Conventional Electrolysis	—	108-208	—	90.0	20.454

The electrolyte (2g/l $CuSO_4$) was pumped up through the glass frit, thus fluidizing the bed. The bed consists of 40 mesh glass ballotini chemically coated with copper. His findings agreed with those reported by Surfleet[9] in that the reduction in p^H increases the rate of copper deposition without affecting the current efficiency. Further he showed that percent of copper removed is a linear function of time of electrolysis for each of currents studied (0.66 A, 1.5 A and 2.7 A). The current efficiency remains constant even when copper concentration reaches ppm levels. In Table – 2, the results of a comparison study of a fluidized bed and a plate electrode has been shown. Figures for a conventional electrolysis operation are also included for comparison. The results of table – 2 show that acceptable rates of removal and power efficiencies may be achieved compared with conventional electrolysis proceedings. Using fluidized bed cell, the theoretical limit of copper concentration can be approached without appreciable loss in current or power efficiency.

As observed from table – 2, using fluidized bed electrode, the theoretical limit of copper concentration can be approached without appreciable loss in current or power efficiency. Fleet has suggested a complete flow-sheet (Fig 1) for the recovery of copper from very dilute solution (1–2 g/l) by using fluidized bed electrode on which he took a patent[10].

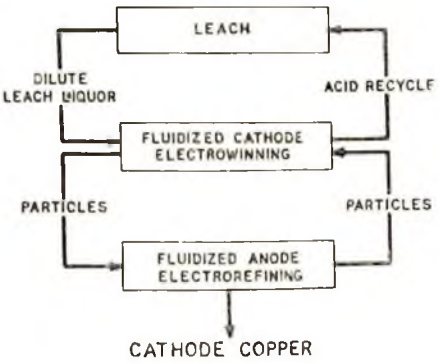


FIG.1 PROPOSED FLOWSHEET FOR FLUIDIZED BED ELCTROLYSIS

This flowsheet is a modified one of that proposed by Surfleet[8]. According to this system the particles subjected to cathode deposition for a period of time become the anode in another cell to be depleted of copper. By proper integration of the circuit these particles would cycle between anode and cathode and on make up would be required. Finally the copper can be plated out onto a plate cathode to yield a high quality, immediately saleable product.

Basing on his priliminary studies Fleet[11] has scaled up the cell capacity to develop an operating concept which might render the process more acceptable to the industry. The perspex cells were 34 × 3 × 1 cm (internal measurements) for each compartment. The bed consisted of copper particles and the current feeder to the cathodic bed was 20 SWG copper wire in the form of a ladder where the anode was an antimonial lead sheet. The anolyte was 1 M H_2SO_4. For fluidized anode studies the current feeder was platinum wire ladder. The electrolyte composition was similar to that of a conventional electrorefinery, i.e. 47g/l copper in 1 MH_2SO_4. Combined cathodic and anodic studies were carried out to examine the feasibility of particle recycling for which two cells were run in series, one with a fluidized cathode and inert plate anode and the other with a fluidized anode and a copper sheet cathode. For the fluidized cathode cell feed liquors containing 1 MH_2SO_4 and 2g l copper were employed with an anolyte composition of 1 MH_2SO_4. For the fluidized anode cell, catholyte and anolyte contained 1 MH_2SO_4 and 50g/l copper. The electrowinning and electrorefining of copper were thoroughly studied and discussed. Several runs in which particles were recycled between cathode fluidized bed and anode fluidized bed were performed. The results show that there is a tendency for the current efficiency of the fluidized cathode to increase as the cell current increases. Further he concluded from his studies that operation of combined electrowinning/electrorefining process of copper using fluidized electrodes, in which particles are recycled from cathodic to anodic to cathodic conditions and so on, is quite feasible.

Haines and Wilkinson[12-14] have studied the electrowinning of copper in much larger scale to examine the industrial feasibility of the fluidized bed electrode system. They started with relatively smaller cells, and larger cells were constructed and the diaphragm areas were increased from 3 cm × 8 cm, through 3 cm × 20 cm and 30 cm × 40 cm to 100 cm × 100 cm. The principal experiments were designed to establish and optimise the current efficiencies at high current intensities. Because, to minimise the total cost of copper production, it is necessary to obtain high current efficiencies for the deposition of copper at high current intensities. With a fluidized bed thickness 0.8 - 2.0 cm, diaphragm area of 30 cm × 40 cm and 100 cm × 100 cm were used at 90-95% current efficiencies at low impurity levels. A 30 cm × 40 cm cell has been operated at 100 A for 100 hr continuously and at 500 A for several hours. A 100 cm × 100 cm cell has been operated successfully at 1000 A for several hours. Using, in the main, beds of 30 cm × 40 cm cross section, they reduced copper concentration from 3000 ppm down to as low as 1 ppm at current densities ranging from 500 to 1000 A m^{-2}. Above a critical minimum copper concentration, current efficiencies were 80-90%. Once down to 100 ppm and at a current density of 1000 Am^{-2}, the current efficiency was 30%. Similar results have also been reported by Surfleet[9] Haines and Wilkinson[14] have also reported the successful operation of a fluidized anode working at 10,000 Am^{-2} for several hours.

Goodridge and Germain[15] studied the performance of fluidized cathodes during the electrowinning of copper from dilute solutions (2g/l). They have given more emphasis on the determination of potential and current distribution within the fluidized electrode, using a reasonably large bed of geometry, capable of being scaled up to pilot plant size. The perspex cell has a rectangular geometry where anode and cathode compartments were separated by a ceramic permeable membrane. The fluidized cathode has a cross sectional area of 0.023 m^2 and a depth of 0.025 m in the direction of current flow and consists of solid copper particles, 500μm dia. The electrolyte used had a nominal composition of 2000 ppm of copper and 1M sulphuric acid. They observed that under the conditions used, copper can be deposited with high current efficiency using a fluidized bed electrode, provided a sufficiently high current density is used. Current efficiency of 95% was obtained at a current density of 2500 Am^{-2}. At constant current density, the electrode becomes increasingly more active near the feeder as the bed expansion is increased.

Conclusion :

The idea of fluidized bed electrode is only reported in late sixtees. During this period, it progressed to a stage where we can expect to adopt it in pilot plant scale. In a fluidized bed electrochemical reactor the effective current conducting area is sufficiently larger to allow the flow of large electric currents in a relatively small reactor volume, without effecting unduly large current densities. Applications for these systems have been proposed in organic electrosynthesis and extractive metallurgy and metal winning. The most attractive aspect of fluidized bed

electrode system is the electrolysis of very dilute solutions (ppm level) with comparable current efficiencies with conventional system. The leach liquors obtained from dump leaching and the waste solutions cannot be taken for direct electrolysis. Because in the deposition of metals from dilute solutions it is necessary to operate at low current density at the electrode surface - otherwise, concentration polarisation leads to low current efficiencies and high power costs. The use of low current intensities with planar electrodes results in expensive plant. But it is possible to recover these metal values using a fluidized bed electrode system. It has already been shown that power costs for directly treating these solutions are acceptable and preliminary estimates of the capital cost of a fluidized bed electrode plant are also encouraging. Not much work has been carried out to apply this system to recover a wide number of metals but limited to few metals like Ni, Zn and Cu. More detailed work has been done on copper extraction. It has already been tried to extract copper from dilute solutions in a size comparable to semi-pilot plant and it is expected that within a limited period a pilot plant will come up. It is realised that more attempts should be made to use this novel technique to extract wide range of metals from dilute leach liquors and effluents.

REFERENCES

1. F. Goodridge, Chem. Process Engng , 49(1968) 93–95 & 100.
2. J. R. Backhurst, F. Goodridge, R. E. Plimley and M. Fleischmann, Nature, 221 (1969) 55–57.
3. J. R. Backhurst, F. Goodridge, R. E. Plimley and M. Fleischmann, J. Electrochem. Soc. 116(1969) 1600–1607.
4. F. Goodridge, D. I. Holden, D. H. Murry and R. E. Plimley, Trans. Inst. Chem. Engg, 49(1971) 128–136.
5. F. Goodridge, D. I. Holden, D. H. Murray and R. E. Plimley Trans. Inst. Chem. Engng, 49(1971) 137–141
6. F. Vergnes et. al. Corrosion (Rueil—Malwaison), 17(1969) 131–36.
7. R. Thangappan et. al., Metal Finishing, 69(1971) 43–45.
8. B. Surfleet, Electricity Council Report, 1970, ECRC/R, 251.
9. D. S. Fleet, Chem. And Ind. (1971) 300–302.
10. D. S. Fleet, Improvement in the recovery of metal U. K. Patent, Applil, 28701/70, 11, Jan. 1970.
11. D. S. Fleet, Chem. Ind. (1972) 982.
12. K. P. Haines and J. A. E. Wilkinson, Trans. Inst. Min. Metal, 81(1972) C 157.
13. K. P. Haines and J. A. E. Wilkinson, Ind. Recovery, 17 (1971) 26.
14. J. A. E. Wilkinson, Trans. Inst. Metal Finish, 49(1971) 16.
15. S. Germain and F. Goodridge, Electrochem. Acta, 21 (1976), 545–550.