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Antimony removal from dilute solutions using a restrained bed electrochemical reactor

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The electrochemical removal of Antimony from 1 M sulphuric acid in a restrained bed reactor was studied in terms of current, flow velocity, bed depth, bead size and pressure drop. Current efficiencies are quoted as a function of current density and information is given so that they may be calculated in terms of the above variables. Experimentally-obtained limiting current densities are compared with calculated values, using empirical formulae from the literature.

1. Introduction

The removal of metal ions from solution by electrochemical means is becoming an increasingly important industrial technique which not only alleviates environmental problems but also recovers in the most desirable form a valuable by-product. Because such metals frequently occur in very dilute solutions, the problem becomes essentially one of designing a reactor capable of efficient mass transport. The deposition and recovery of dilute Cu^{++} ions in forced-flow parallel plate reactors has been described elsewhere [1, 9] and also in trickle flow porous bed reactors [2]. Several other authors [3, 4, 5] have described the use of fluidized beds for the electrowinning of Cu^{++} from dilute solutions. A survey of reactor designs with qualitative data relating to them is available elsewhere [6]. The present work describes metal ion removal in a 'restrained bed' reactor operating under forced flow conditions. This, which is shown in Fig. 1, is not unlike a fluidized bed cell in construction, though, as the name implies, the particles remain continuously in physical contact, being prevented from fluidizing by a mesh over their surface. While forced-flow packed or restrained beds have been mentioned in the literature, this has been wholly in the context of patents [8, 11, 12, 13] with little or no quantitative data, whilst the academic studies mentioned above, as well as those of Sioda [7] relating to stacked gauzes, refer to very different flow regimes.

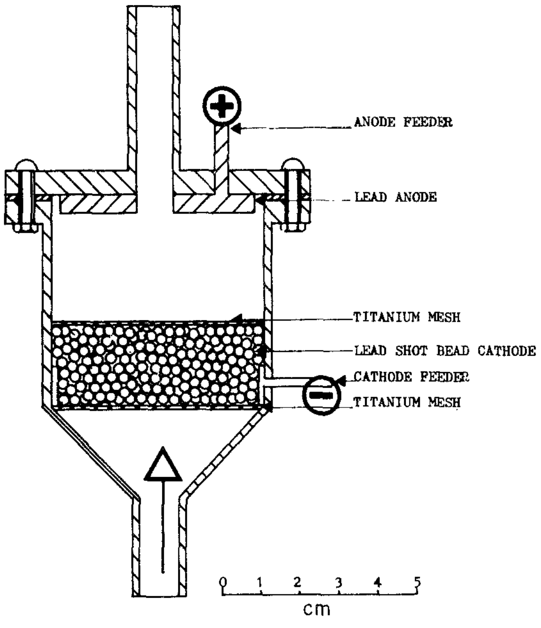

Fig. 1. Restrained bed cell.

Data published in patent form [8] suggest that this type of cell may possess mass-transfer characteristics superior to those of a fluidized bed, although it must be conceded that the latter can offer certain advantages such as better form of electrodeposit etc.

The reaction studied here is the deposition of trivalent antimony, a metal present in a variety of industrial waste streams, notably those occurring in electrorefining. While, from a completely academic point of view, it is not the most straightforward reaction, enough information has been gathered to test the performance of a restrained bed reactor and to compare it with theory.

2. Experimental

2.1. *Description of cell and flow system*

4000 ml of the stock solution of 1 M sulphuric acid containing 100 p.p.m. antimony were held in a polythene reservoir and circulated through the cell by means of a Beresford model P. V. 101 pump with polypropylene impeller and casing. A reflux condenser, connected in series with the pump, was used to control the temperature of the electrolyte at 30°C (±5°C). Gases produced by electrolysis were vented to the atmosphere via a wash bottle containing an aqueous solution of iodine and potassium iodide intended to remove any stibine formed in the cell. The flow rate of electrolyte through the cell was controlled by means of a Variac connected to the pump motor.

The cell was fabricated from tubular and sheet perspex and consisted essentially of three sections. The first section, a 45° diverging cone, was designed to provide uniform flow through the cathode. The cathode, consisting of lead shot, was retained in the 50 mm diameter cylindrical portion of the cell by means of titanium mesh placed above and below the cathode material. Electrical contact to the cathode was provided by a sheet of lead 10 mm deep placed around the inner circumference of the cell. The circular sheet lead anode was placed above the cathode and was provided with a central hole to permit flow of electrolyte through the cell. The experiments were carried out using cathode bed depths of 10, 20 and 40 mm and cathode bead sizes of 1·11 and 2·60 mm diameter. Electrical power was supplied by a Farnell 5A stabilized d.c. source operated in a constant current mode. Current and voltage measurements were taken using Sangamo-Weston (secondary standard) meters. Pressure drops across the cell were measured using a differential mercury manometer. The cell is shown in Fig. 1.

2.2. *Analysis*

The stock solutions of 1 M sulphuric acid, containing 100 p.p.m. antimony, were prepared from AnalaR sulphuric acid, AnalaR antimony potassium tartrate and distilled water. The antimony concentration of the solution was determined using a Perkin Elmer Model 303 atomic absorption spectrophotometer at a wavelength of 2176 Å. The instrument was calibrated against standard solutions of 1 M sulphuric acid containing known amounts of antimony before each series of analyses was undertaken. Analysis of the evolved gases for stibine was carried out colorimetrically. The solution from the gas washing bottles was decolourized with ascorbic acid and the stibine determined as the yellow potassium iodo-antimonate (KSb I_4) complex using an EEL* visible spectrophotometer.

2.3. *Nature of deposit*

The metallic antimony deposited on the cathode was mainly in the form of a black sludge which was easily removed from the cathode material by washing. Stibine evolution in the system was found to be of the order of one thousandth of that of metallic antimony deposited at the

Table 1. Analysis of reduction products of Sb^{+++}

Current	*Sb Deposited*	*Sb as* SbH_3 *evolved*	$\frac{Sb}{Sb \text{ as } SbH_3}$
5 A	110 mg	0·10 mg	1100
1 A	112 mg	0·13 mg	861
0·25 A	68 mg	0·60 mg	1133

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* Evans Electroselenium Ltd.

cathode over the range of currents used. The predominating reaction in the cell was, based on these results (Table 1), taken to be:

$$Sb^{+++} + 3e \rightleftharpoons Sb$$

Efficiencies quoted in the figures are based on the three electron reduction reaction.

3. Results

The reactor performance was studied by measurement of Sb^{+++} concentration reduction with time as a function of the following variables.

(i) Current,
(ii) flow rate through the cell,
(iii) bed depth,
(iv) bead size,

in the range 100 to 5 p.p.m. Sb^{+++}.

The results of these experiments are shown in the figures where current densities are expressed as $mAcm^{-3}$ of cathode bed volume.

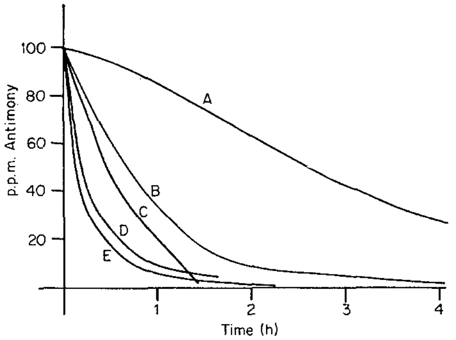

Fig. 2. Sb concentration versus time. Flow rate 227 ml s^{-1}, bed depth 20 mm, bead size 2·6 mm. (A) 0·25 A, (B) 0·5 A, (C) 1·0 A, (D) 2·0 A, (E) 5·0 A.

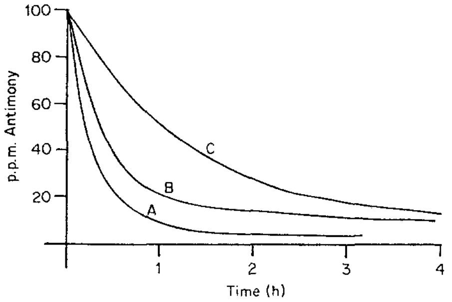

Fig. 3. Sb concentration versus time. Current 2 A, bed depth 20 mm, bead size 2·6 mm. (A) 277 ml s^{-1}, (B) 204 ml s^{-1}, (C) 144 ml s^{-1}.

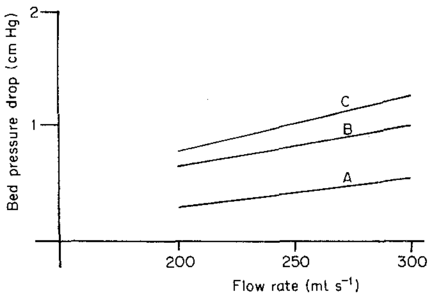

Fig. 4. Pressure drop across cell versus flow rate. (A) 2·6 mm beads 10 mm deep, (B) 2·6 mm beads 20 mm deep, (C) 1·11 mm beads 20 mm deep

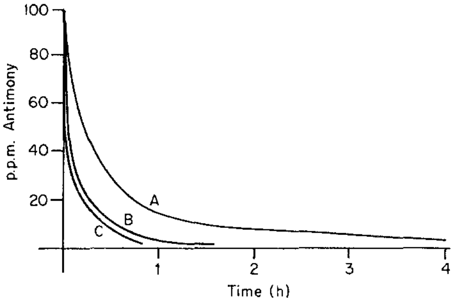

Fig. 5. Sb concentration versus time. Current 5 A, 2·6 mm beads, 277 ml s^{-1}. (A) = 10 mm bed depth, (B) = 20 mm bed depth, (C) = 40 mm bed depth.

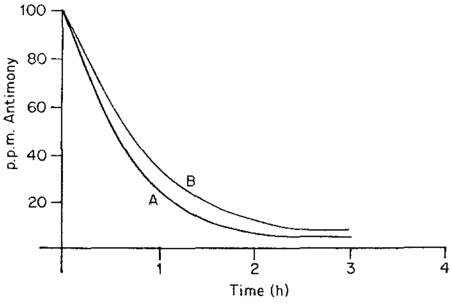

Fig. 6. Sb concentration versus time. Current 0·5 A, 20 mm bed depth, 277 ml s^{-1}. (A) = 2·6 mm beads, (B) = 1·11 mm beads.

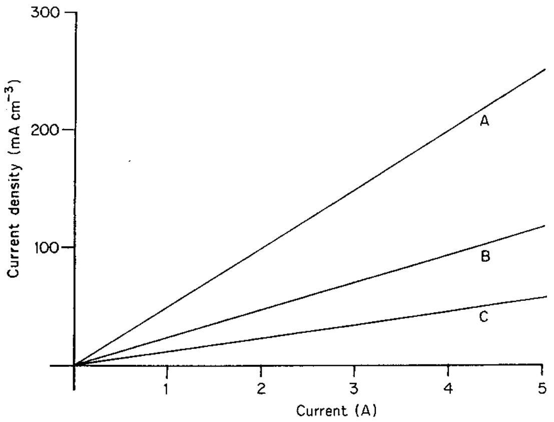

Fig. 7. Current versus current density (mA cm^{-3}). 2·6 mm diameter bead. (A) = 10 mm bed depth, (B) = 20 mm bed depth, (C) = 40 mm bed depth.

The current efficiency with which the metal is removed from solution is shown in Figs. 8 and 9.

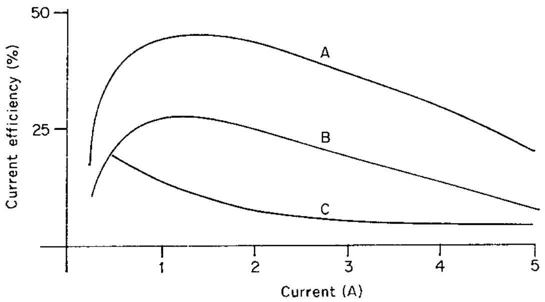

Fig. 8. Efficiency at 100 p.p.m. versus current. 20 mm bed depth, 2·6 mm beads. (A) 277 ml s^{-1}, (B) 204 ml s^{-1}, (C) 144 ml s^{-1}.

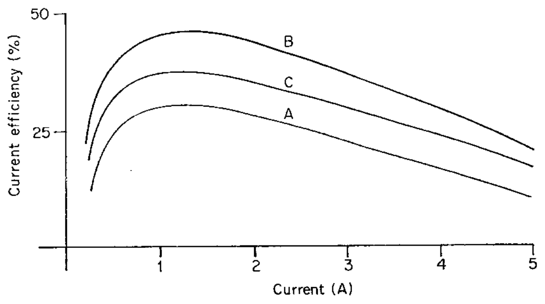

Fig. 9. Efficiency at 100 p.p.m. versus current. 2·6 mm bead, 277 ml s^{-1}. (A) 10 mm bed depth, (B) 20 mm bed depth, (C) 40 mm bed depth.

4. Discussion

The inherent difficulty of analysing results obtained on three-dimensional electrodes is well-known, for the inequality of metal-solution potential across the bed can lead to differences in rates of reaction, or even the reversal of their direction. In the present reaction

$$Sb^{+++} + 3e \rightleftharpoons Sb$$

$$E_{rev} = 0{\cdot}40 \text{ V for } [Sb^{+++}] = 100 \text{ p.p.m.}$$

The metal, once formed from the ion, will rapidly re-dissolve, if removed from the areas of 'cathodic protection'. Likewise hydrogen evolution will certainly occur at the more cathodic part of the bed. Thus low currents will lead to antimony re-dissolution and high currents will lead to the hydrogen evolution reaction which explains the low current efficiencies. In the majority of cases, however, the system is mass transport-controlled, and log concentration versus time plots are rectilinar.

Another feature of the plots, especially at low current densities (0·25 A), is an induction period. This is due to reduction of oxides, formed on the lead cathode between successive runs, which must be reduced to metallic lead before the electrodeposition of antimony can occur. This phenomenon is reflected in the fact that initial cell voltages of low current density runs decreased by as much as 300 mV to an equilibrium voltage within the first thirty minutes of the experiment.

It may be asked why it is apparently impossible to lower the Sb^{+++} concentration below 5 p.p.m. It appeared that this was an equilibrium concentration at which re-dissolution of the metal took place at the same rate as the deposition. To confirm this, a 'clean' system was operated for one hour during which the antimony concentration remained at zero. 100 mg of metallic antimony was added to the system, whereupon the Sb^{+++} concentration rose rapidly to 25 p.p.m. Electrolysis of the cell again reduced the antimony concentration to 5 p.p.m. after two hours, but subsequent electrolysis over a further 6 h period achieved no subsequent reduction. The existence of such 'lower limits' has also been observed in other electrochemical metal-removal systems [15]. Granted the complex chemistry of the situation (not to mention a minor amount of anodic oxidation $Sb^{+++} \rightarrow Sb^{+++++}$ at the counter electrode), analysis of the results is difficult, several attempts having been made by Gurevich [10]. Colquhoun-Lee [14] has reviewed the literature relating to hydrodynamic relationships in packed beds and finds that the expression:

$$i = 1{\cdot}24\, C_b\, A\, n\, F \frac{(1-E)^{0\cdot39}}{Dp^{0\cdot39}}\, V^{0\cdot61}\, \frac{(e)^{0\cdot27}}{u}\, D^{2/3}$$

offers the best correlation

where: A = electrode surface area (cm^2)
n = no. of electrons transferred per molecule
F = Faradays constant $\left(96\,500 \frac{C}{g.equiv}\right)$
C_b = conc. of reacting species (gmol cm^{-3})
e = density (g cm^{-3})
u = dynamic viscosity (Poise)
D = diffusivity of reacting species ($cm^2\ s^{-1}$)
Dp = particle characteristic dimension (cm)
E = packing void fraction
V = fluid velocity (cm s^{-1})
i = limiting current (amps)

We have applied this to our results and the i_{lim} thus calculated is expressed in Fig. 10.

From these results the diminishing benefits of thicker beds are clearly demonstrated. However, as a study of the data shows, in this particular case the effect is not due to the change in bed solution potential discussed by Armstrong *et al.* [16] but due to the re-dissolution phenomenon mentioned above.

In spite of this, the results indicate that electrochemical removal of Sb^{+++}, in the condition here described, and using a forced-flow packed bed, is a potentially attractive and economically viable means for treatment of this type of effluent stream.

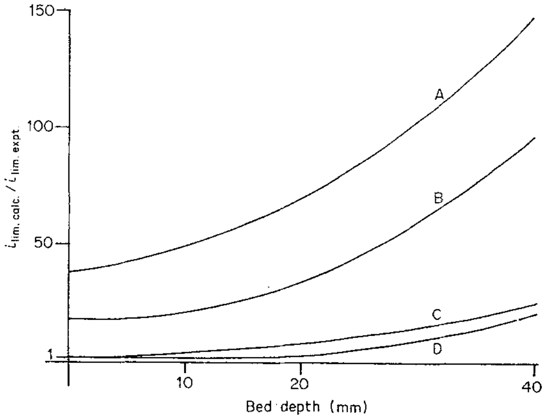

Fig. 10. $\frac{i_{lim.calc.}}{i_{lim.expt.}}$ versus bed depth. (A) = 0·25 A, (B) = 0·5 A, (C) = 2·0 A, (D) = 5·0 A.

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