SHORT COMMUNICATION

Reticulated vitreous carbon cathodes for metal ion removal from process streams
Part III: Studies of a single pass reactor

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1. Introduction

The literature on metal ion removal from aqueous electrolytes using cells with three-dimensional electrodes is extensive [1–7] and some such cells have found success in industrial practice [7, 8]. Most of the literature, however, considers those cells where a high conversion requires substantial recycle of the electrolyte; moreover, where a high conversion in a single pass through a cell has been reported, the authors have generally employed low flow rates in a flow-through reactor [1, 9]. In other cases, the use of low porosity electrode materials led to pressure drop limitations in the flow-by mode. The first two papers of this series [10, 11] defined the mass transport characteristics for several grades of vitreous carbon and described the study of a batch recycle system for the removal of Cu(II) from acidic sulphate solutions using a flow-by cell with a reticulated vitreous carbon cathode. It was confirmed that a reticulated vitreous carbon cathode allows efficient metal ion removal down to low reactant concentrations, for example, from 10 p.p.m. to < 0.1 p.p.m.

The fractional conversion, X_A, for a plug flow electrolytic cell operating under mass transport control is given by [8]

$$X_A = 1 - \exp\left(-k_m A_e L/v\right) \qquad (1)$$

where k_m is the mass transfer coefficient (m s^{-1}), A_e is the specific surface area (m^2 m^{-3}), v is the mean linear flow velocity (m s^{-1}) and L is the electrode length [8]. Substitution of the values determined for $k_m A_e$ [10, 11], led to the conclusion that it should be possible to construct a compact, flow-by reactor giving high conversions at moderate flow rates. The purpose of this study was to test the performance of a cell with a 400 mm long vitreous carbon cathode; to allow more detailed examination, the electrode was constructed from eight segments which were controlled independently.

2. Experimental details

Experiments were carried out at 298 K with deo-xygenated solutions of copper sulphate in 0.5 M sodium sulphate adjusted to pH 2 with sulphuric acid; the anolyte was always 0.5 M sulphuric acid. The reagents were AR grade. The procedure for atomic absorption analysis and much of the equipment have been described previously [1].

The cell is shown in Fig. 1. It was constructed from four polypropylene blocks, each 620 mm × 100 mm × 12 mm. The anode was a Pb/6% Sb plate (400 mm × 50 mm) sunk into one of the polypropylene end plates so that its surface was flush with the
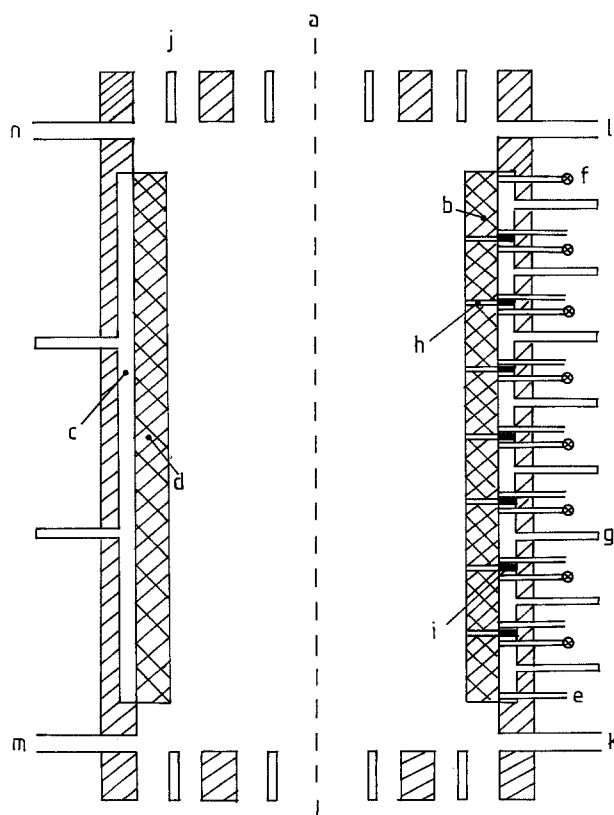

Fig. 1. Sectional view of the segmented cathode cell showing (a) Nafion® 417 membrane, (b) reticulated vitreous carbon cathode segment (50 mm × 50 mm × 12 mm), (c) Pb/Sb anode plate, (d) reticulated vitreous carbon packing within anolyte chamber, (e) reference electrode probe, (f) solution sampling port, (g) stainless steel cathode current collector, (h) plastic mesh insulator, (i) Viton insulator, (j) Viton gasket, (k) catholyte entry port, (l) catholyte exit port, (m) anolyte entry port, (n) anolyte exit port.

polymer surface; there were two current feeders. The cathode current collector system comprised eight separate stainless steel plates, each 50 mm × 48 mm, mounted within the other polypropylene end block and with separate electrical contacts. Insulating Viton strips were positioned between each steel plate. Each reticulated vitreous carbon block, 50 mm × 50 mm × 12 mm, was cemented to a steel plate with a conducting carbon cement (Leit-C from Agar Aids); the eight reticulated vitreous blocks, insulated from each other with thin polymer nets, fitted tightly into the catholyte compartment formed within a third polypropylene block. The fourth formed the anolyte compartment which was packed with reticulated carbon to support the membrane. Unlike the earlier cell [10], neither catholyte nor anolyte chambers had 'calming sections' at the entry and exit. A Nafion® 417 cationic membrane separated the anolyte and catholyte and the four compartments, together with the membrane were gasketed with 1 mm silicone rubber sheet. The cell was closed with steel bolts and sealed around the electrical contacts with Viton O-rings and polypropylene washers. 'Luggin capillaries' to each segment of reticulated vitreous carbon were formed by drilling 3 mm holes through the polypropylene end plate and each steel current collector and these holes were connected via Tygon tubing to an eight tap reference electrode compartment containing a commercial aqueous saturated calomel electrode. A second, 3 mm hole allowed sampling of the solution 3 mm before the outlet edge of each cathode segment. The equipment for independent potentiostatic operation of the segments was built in house. The electrolyte flow system has been described previously [10].

Table 1. $k_m A_e$ estimated for each of the reticulated vitreous carbon (100 p.p.i.) cathode segments at $v = 0.01\,m\,s^{-1}$.

Electrode segment	$k_m A_e^*/s^{-1}$	$k_m A_e^\dagger/s^{-1}$
1	0.070	0.068
2	0.069	0.064
3	0.076	0.060
4	0.076	0.070
5	0.077	0.079
6	0.076	0.065
7	0.071	0.073
8	0.071	0.070
Average value	0.073	0.069
From [10]	0.073	0.073

* From limiting currents with a single cathode segment in operation, i.e. $k_m A_e = I_L/2FcV_e$.
† From concentration vs time curves during simultaneous operation of all cathode segments, i.e. $c_{out} = c_{in} \exp(-k_m A_e L/v)$.

3. Results and discussion

In the first set of experiments, the catholyte was 63 p.p.m. (1 mM) Cu(II) in sodium sulphate, pH 2 and the flow rate was $10\,mm\,s^{-1}$. The electrode segments were operated singly at a potential of -0.50 V/SCE (when the reduction of Cu(II) is mass transport controlled), with the other seven on open circuit. Values of $k_m A_e$ were estimated from these limiting currents using Equation 1 of [10]. The results are reported in Table 1; electrode segments are labelled 1-8 from inlet to outlet. It can be seen that the average value of $k_m A_e$ agrees well with that reported earlier [10]. The first two and the last two segments give slightly lower values than the middle four, probably indicating small entry
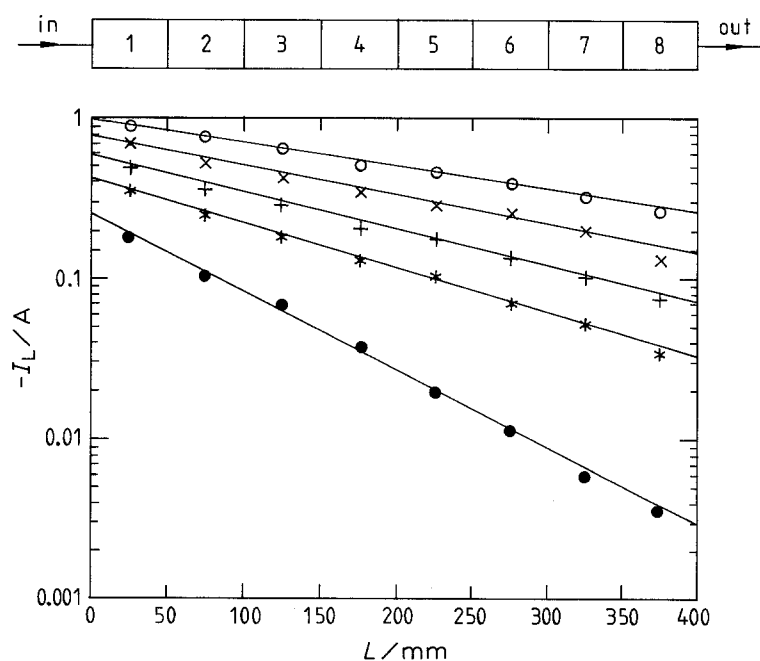

Fig. 2. Plots of log I_L against L for the cell with all eight segments operating simultaneously. The solution is 63 p.p.m. (1 mM) Cu(II) in 0.5 M sodium sulphate, pH 2. Potential: -0.5 V/SCE. Linear flow velocity of the electrolyte/mm s^{-1}: (●) 3.5, (★) 10.3, (+) 16.3, (×) 28.7 and (○) 44.
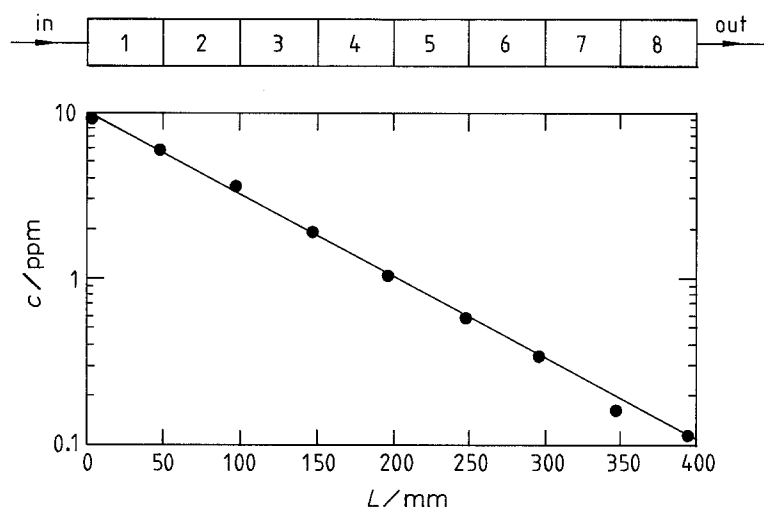
Fig. 3. Plot of [Cu(II)] against L. Inlet solution: 10 p.p.m. Cu(II) in 0.5 M sodium sulphate, pH 2. Electrolyte linear flow velocity 3.5 mm s^{-1}. Cathode potential: -0.5 V/SCE.

and exit effects; overall, however, the mass transport behaviour appears to be very uniform.

The current distribution was measured by operating all the cathode segments simultaneously. The limiting tertiary current distribution for several mean linear flow rates, reported as plots of log I_L against L, are shown in Fig. 2. It can be seen that the plots are linear and that, at the slowest flow rate (3.5 mm s^{-1}), the currents decrease by almost two orders of magnitude through the cell. At higher flow rates, the conversion through the cell decreases as predicted by Equation 1.

Applying -0.5 V to all cathode segments and passing a solution 10 p.p.m. in Cu(II) in sodium sulphate, pH 2, at 3.5 mm s^{-1}, the solution was sampled throughout the cell and the concentrations of Cu(II) were determined by atomic absorption spectroscopy. The results are presented as a plot of [Cu(II)] against L in Fig. 3; it can be seen that the 400 mm reticulated vitreous carbon electrode is successful in reducing the Cu(II) content from 10 p.p.m. to ~ 0.1 p.p.m. in a single pass, i.e. the fractional conversion is ~ 0.99. The current efficiency was 69% and the normalised electrolytic energy consumption for the cell (defined as

the energy consumed in reducing the concentration of reactant tenfold, i.e. 10 p.p.m. $\rightarrow$ 1 p.p.m., in unit volume of solution using a unit electrode volume [12]) of unit volume was < 30 Wh m^{-3}.

Further analysis of the system at the slow flow rate was made difficult by the accuracy of the atomic absorption analysis when the concentration approached 0.1 p.p.m. When the flow rate was increased and the cell was operated in the batch recycle mode, it was possible to monitor the c against t behaviour at each of the sampling ports. Figure 4 shows the results for the first seven sampling ports during an experiment where $v = 10$ mm s^{-1}. The concentrations show the expected exponential decay with time and the slopes may be used to estimate further values of $k_m A_e$; these are also reported in Table 1. The agreement with the data calculated from the limiting currents is good.

Overall, the above results show that the scale-up of the cell from an electrode length of 50 mm to 400 mm is possi̇b̤l̤e and that the behaviour of the larger cell is well described by plug flow reactor expressions. Scaling the cathode further to a 1 m × 1 m sheet of 12 mm thick reticulated vitreous carbon sheet in the equiva-
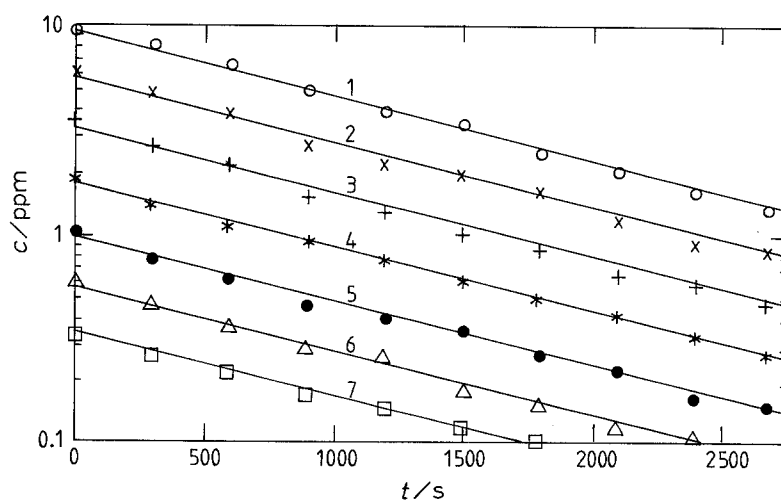

Fig. 4. Plot of [Cu(II)] at the first seven sample ports against time during the batch recycle treatment of a 10 p.p.m. solution of Cu(II) in 0.5 M sodium sulphate, pH 2. Linear flow velocity 10 mm s^{-1}. Cathode potential: -0.5 V/SCE. The electrode number is shown on each line.

lent cell, would allow the removal of 99% of the metal ion from an effluent flowing at a rate of $1\,m^3\,h^{-1}$ in a single pass. Larger volumes would best be handled by (a) increasing the thickness of the reticulated vitreous carbon although, inevitably, potential drop through the cathode would limit the useful thickness (b) running several cathodes in parallel; in this way, a compact unit to handle $10{-}100\,m^3\,h^{-1}$ could be designed. It should be emphasized that reticulated vitreous carbon cathode is most advantageous for the treatment of solutions with low concentrations of the metal ion to be removed. At high concentrations, massive metal deposition in the three dimensional structure quickly degrades its performance, as is the case with all three dimensional electrodes. Hence, for more concentrated solutions, another cell design should be used for the first stage of metal removal and the reticulated vitreous carbon cell should be used only for the final polishing of the effluent before discharge.

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