

Reticulated vitreous carbon cathodes for metal ion removal from process streams

Part II: Removal of copper(II) from acid sulphate media

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The performance of cells with reticulated vitreous carbon cathodes for the removal of low levels of copper ions from aqueous, acidic sulphate media is described. During the batch recirculation of nitrogen-sparged, sodium sulphate solutions, pH 2, the copper ion concentration may be reduced from 10 p.p.m. to < 0.5 p.p.m. or from 2.5 p.p.m. to < 0.1 p.p.m. with overall current efficiencies of 84% and 42%, respectively. The influence of solution flow rate through the cathode and the choice of the grade of the reticulated carbon is discussed. The removal of copper ions from solutions of low ionic strength, saturated with air and/or containing chloride ion is also investigated.

1. Introduction

In the previous paper, mass transport to reticulated vitreous carbon electrodes was discussed [1]. Reticulated vitreous carbons have a regular structure, a high surface to volume ratio, a high porosity, good electrical conductivity and reasonable structural properties; they seem very well suited as cathodes in cells for the removal of metal ions from solution. Indeed, earlier papers have discussed cells with such cathodes for this application [2-5]. In this series of papers, the objective is to re-examine the use of reticulated vitreous carbon electrodes, particularly for the treatment of solutions containing only very low concentrations of metal ions. In addition, the intention is to emphasize real, practical situations and hence to investigate, for example, the problems met due to oxygen and complexing agents in solution, pH changes at the cathode surface, low conductivity media and mixtures of metal ions.

In this paper, the system studied is copper(II) in sodium sulphate, pH 2. Emphasis is placed on the treatment of solutions with less than 10 p.p.m. copper ion in a batch recirculation system. The investigation encompasses the influence of oxygen, low sulphate concentration and the presence of various amounts of chloride ion. Copper ion in acid sulphate solutions has been a popular system for testing cells with three dimensional electrodes [2, 6-11].

2. Experimental details

The procedures and equipment including the flow-by, membrane cell with a rectangular block of reticulated vitreous carbon as the cathode were described in part I of this series [1].

The analysis for copper(II) was normally carried out by atomic absorption spectroscopy using an oxygen/acetylene flame but on some occasions the conclusions were checked with an ion selective electrode [13]; good agreement was always found. Some comment about the analysis at low levels of copper(II) is necessary. Reliable analysis is readily achieved when the Cu(II) concentration is above 0.5 p.p.m. To obtain reliable results in the range 0.05-0.5 p.p.m., it was essential to set up the instrumentation with very great care and, even then, the lowest detection limit varied from day to day. These difficulties have led us to report our minimum copper(II) levels in the form, < x p.p.m. where this value can be quoted with a high level of confidence.

3. Results and discussion

In the initial experiments, the medium was nitrogen-purged, 0.5 mol dm⁻³ sodium sulphate, pH 2. Typically, controlled potential electrolysis were carried out at -500 mV and the depletion of the copper ion, the cell current and voltage and the charge passed were

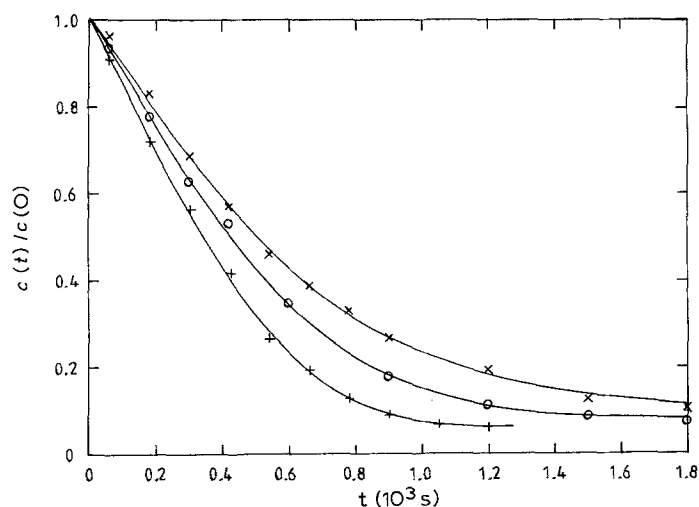


Fig. 1. Normalized copper concentration against time curves for a $0.03 \text{ mmol dm}^{-3}$ (2 p.p.m.) Cu^{2+} in a nitrogen purged 0.5 mol dm^{-3} sodium sulphate, pH 2 solution at a 100 p.p.i. reticulated vitreous carbon foam electrode. Mean linear flow rates of 0.042 (x), 0.083 (O) and 0.125 m s^{-1} (+) m s^{-1} . Potential -500 mV/SCE . $T = 298 \text{ K}$.

monitored as a function of time. Figure 1 shows normalized concentration as a function of time for three electrolyses carried out at different catholyte flow rates; the initial concentration of copper(II) was 2 p.p.m. Other experiments examined the influence of the initial copper ion concentration and the grade of reticulated vitreous carbon and some data from these electrolyses are collected in Table 1. In all cases the copper ion concentration drops exponentially with time [1] and the system may be modelled as a simple batch system. The following conclusions may be drawn:

(i) Under a range of conditions, the concentration of copper ion may be decreased to below 1 p.p.m. and, at least with selected conditions, the concentration may be reduced to below 0.1 p.p.m. which was the lowest level which could be determined reliably with the analytical equipment available.

(ii) The most rapid rate of removal of copper ions is achieved with the smallest pore size reticulated vitreous carbon, i.e. 100 p.p.i., and a high electrolyte flow rate. With a flow rate of 0.125 m s^{-1} , the electrode material achieves a normalized space velocity [12], of approximately $400 \text{ m}^3 \text{ m}^{-3} \text{ h}^{-1}$ (based on the volume of the cathode) even with an initial copper ion concentration of 2 p.p.m., a figure which compares well with other effluent treatment technologies [12]. The energy consumption for the reduction in the copper ion concentration from 2 to 0.2 p.p.m. under these conditions is

4.7 Wh m^{-3} . The normalized power consumption [14] (i.e. the power required to remove 90% of the copper(II) from unit volume of solution using a unit volume cathode in unit time) is 1.92 kW m^{-3} .

(iii) The current efficiency for copper removal is high provided that the concentration of copper ion is above 5 p.p.m. Below this level, the current efficiency begins to tail off although it remains reasonable. The loss in current efficiency is presumably due to incomplete removal of oxygen from the solution.

The $I-E$ curves at the rotating disc electrode [1] suggested that if oxygen is present in the solution, the performance of the cell operated at -500 mV would deteriorate markedly. Figure 2 shows data for two experiments where the initial concentration of copper ion is 25 p.p.m., one where the solution is nitrogen-sparged and the other where it is air-sparged. From Fig. 2a, it can clearly be seen that the presence of oxygen has almost no influence on the rate at which the copper ion is removed from solution; in both electrolyses, the copper ion concentration decays exponentially to below 1 p.p.m. On the other hand, the current through the cell is much higher when oxygen is present, see Fig. 2b, and this inevitably leads to a decrease in the current efficiency, see Fig. 2c. This, in turn, must increase the energy consumption of the process although not necessarily to an unacceptable extent.

The effect of oxygen was probed further in a series

Table 1. The removal of copper ion from 0.5 mol dm^{-3} sodium sulphate, pH 2 at reticulated vitreous carbon cathodes

Initial [Cu(II)] (p.p.m.)	Grade RVC (p.p.i.)	v (m s^{-1})	Time for 90% removal (10^3 s)	Current eff. for 90% removal (%)	Final [Cu(II)] (p.p.m.)
52	100	0.042	1.35	85	< 0.4
8	100	0.083	1.08	61	< 0.4
	60	0.083	3.12	53	< 0.4
	30	0.083	7.38	41	< 0.5
	10	0.083	9.18	42	< 0.7
2	100	0.042	1.94	28	< 0.1
	100	0.084	1.18	32	< 0.1
	100	0.125	0.88	49	< 0.1

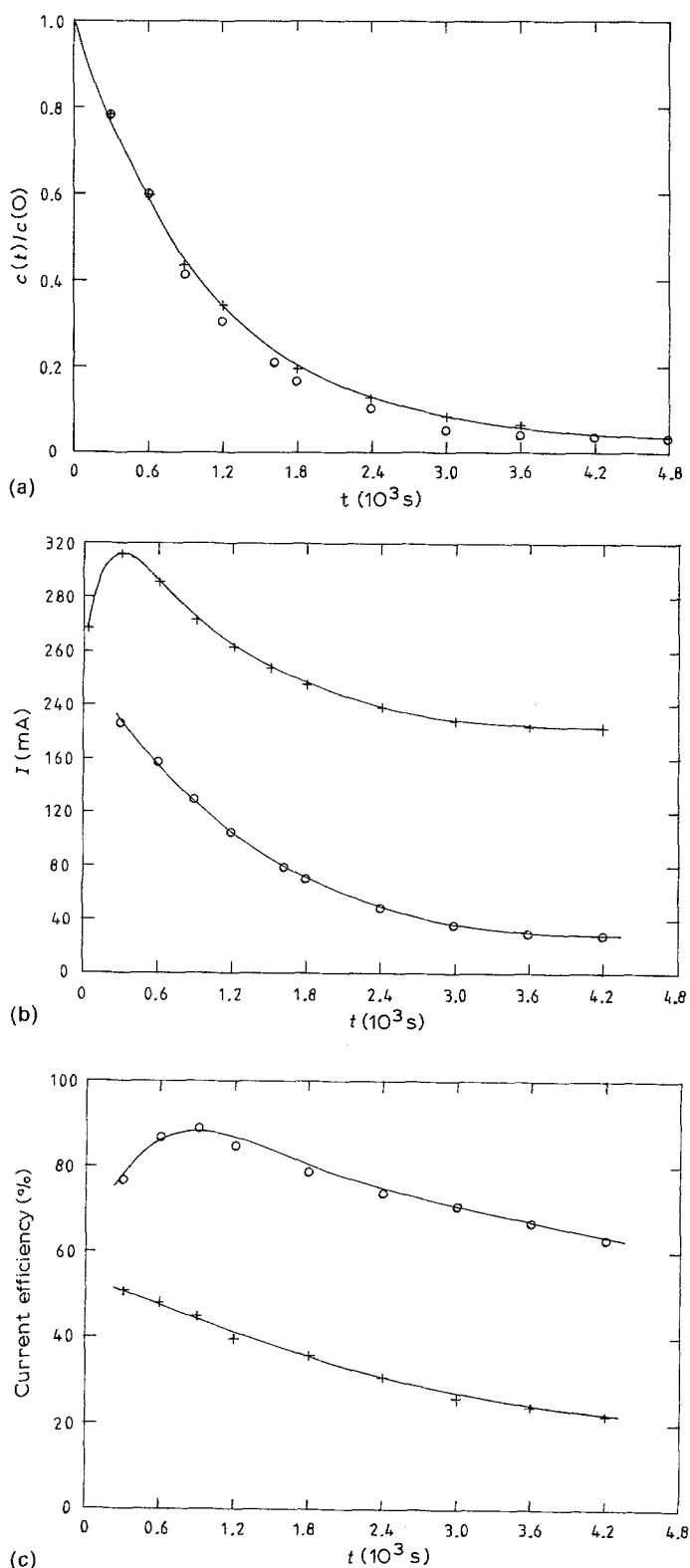


Fig. 2. (a) Normalized copper concentration against time curves for a $0.39 \text{ mmol dm}^{-3}$ (25 p.p.m.) Cu^{2+} air saturated (+) and nitrogen purged (O) 0.5 mol dm^{-3} sodium sulphate, pH 2 solutions at a 60 p.p.i. reticulated vitreous carbon foam electrode. Mean linear flow rate 0.083 m s^{-1} . Potential -500 mV/SCE . $T = 299 \text{ K}$. (b) Current against time curves for the controlled potential electrolysis at -500 mV/SCE in (a). (c) Current efficiency against time curves for the controlled potential electrolysis at -500 mV/SCE in (a).

of experiments carried out at several potentials and the results are reported in Table 2. Again, it can be seen that the presence of oxygen decreases the current efficiency and hence increases the energy consumption. On the other hand, the presence of oxygen never influences the ability of the reticulated carbon cathode to reduce the copper(II) rapidly to below 0.1 p.p.m. It can also be seen that the current efficiency can be improved by making the cathode potential less negative. Apparently, at -0.4 V the deposition of copper remains mass transport controlled (since the time for

90% depletion remains identical to that at -0.5 V) but the adverse effects of the oxygen in solution are much decreased. Indeed, it appears to be a better choice for cell operation. The current efficiency is further improved by operation with a cathode potential of -0.3 V but this is at the cost of a slower removal of the copper ion because the reduction is no longer under complete mass transport control. In practice, this would increase the investment cost since it would be necessary to employ a bigger cell. In optimizing the economics of the process, it would be

Table 2. The influence of oxygen on the removal of copper ion from 0.5 mol dm^{-3} sodium sulphate, pH 2. 100 p.p.i. reticulated vitreous carbon. Linear flow rate: 0.083 m s^{-1} . Temperature: 296 K.

Initial [Cu(II)] (p.p.m.)	O_2 present	$-E$ (V/SCE)	Time for 90% removal (10^3 s)	Current eff. for 90% removal (%)	Energy Consumption for 90% removal (Wh m^{-3})	Final [Cu(II)] (p.p.m.)
10	No	500	1.05	62	23	< 0.1
	Yes	500	1.11	22	92	< 0.1
	Yes	400	1.26	69	25	< 0.1
	Yes	300	2.52	66	23	< 0.1
2	No	500	1.14	35	10	< 0.1
	Yes	500	1.16	7	46	< 0.1
	Yes	400	1.08	44	11	< 0.1
	Yes	300	2.54	70	2.3	< 0.1

necessary to consider the relative merits of reducing cell costs or energy consumption (i.e. to trade initial vs running costs). Operating on the 2 p.p.m. copper ion solution with a potential of -0.4 V , the presence of oxygen at a level resulting from air saturation leads to an energy consumption for a 90% decrease in copper of 11 Wh m^{-3} and a normalized power consumption of 3.7 kW m^{-3} .

A further series of experiments addressed the effects of chloride ion (a species capable of acting as a complexing agent for copper ions even at pH 2) on the removal of copper ion from nitrogen sparged, 0.5 mol dm^{-3} sodium sulphate, pH 2. Preliminary experiments with a rotating disc electrode confirmed that on addition of chloride, the reduction of copper(II) occurs in two, one electron steps. The potential required for the deposition of copper becomes more negative but the shift is small; at all chloride concentrations investigated, -500 mV remains in the mass transport controlled region and this was again the potential used for the electrolyses. Figure 3 shows plots of the normalized concentration versus time for four solution with different concentrations of chloride ion. It can clearly be seen that the rate of copper ion removal is independent of the chloride ion concentration. In addition, the copper ion concentration can always be reduced to below 0.1 p.p.m. There are, however, some variations in the current efficiencies, see

Table 3; initially, it increases before passing through a maximum and decreasing again at very high chloride ion concentrations.

A final series of experiments examined the possibility of removing copper ion from solutions of low ionic strength. Electrolyses were carried out on solutions containing 2 p.p.m. copper(II) in 0.01 mol dm^{-3} sulphuric acid (but without the addition of sodium sulphate). The performance in terms of the minimum copper ion level, the current efficiency and the time for 90% removal of the copper ion were unaffected by the decrease in the ionic strength. On the other hand, the cell voltage does increase and this degrades other figures of merit for the process.

4. Conclusions

It has been demonstrated that it is possible to process solutions of copper(II) in various acid sulphate media and to achieve copper ion levels below 0.1 p.p.m. with excellent cell performance. Air saturation of the solutions had only minor adverse effects on the process performance although it was highly advantageous to operate at a cathode potential of -0.4 V . Chloride ion and decreasing the ionic strength had no adverse effects.

The normalized space velocity of cells with reticulated carbon cathodes was high compared with

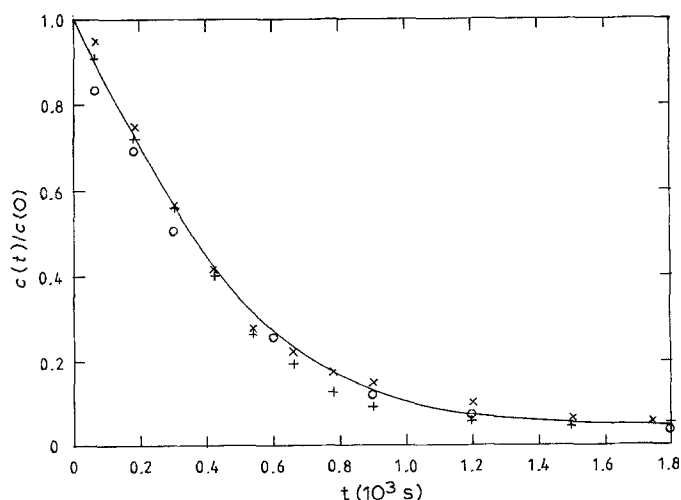


Fig. 3. Normalized copper concentration against time curve for a controlled potential electrolysis at -500 mV/SCE on a 100 p.p.i. reticulated vitreous carbon foam electrode in a nitrogen purged 0.5 mol dm^{-3} sodium sulphate, pH 2 solution containing: (+) 1.7 p.p.m. Cu^{2+} , 0 p.p.m. Cl^- ; (x) 2.3 p.p.m. Cu^{2+} , 1000 p.p.m. Cl^- ; (O) 4.1 p.p.m. Cu^{2+} , 40000 p.p.m. Cl^- . With mean linear flow rate: 0.125 m s^{-1} and $T = 297 \text{ K}$.

Table 3. The influence of chloride ion on the removal of copper ion from nitrogen purged 0.5 mol dm^{-3} sodium sulphate, pH 2. 100 p.p.i. reticulated vitreous carbon cathode. Linear flow rate: 0.125 m s^{-1} . Temperature: 296 K.

[Cl ⁻] (p.p.m.)	Initial [Cu(II)] (p.p.m.)	Time for 90% removal (10 ³ s)	Current eff. for 90% removal (%)	Final [Cu(II)] (p.p.m.)
0	1.7	0.90	49	< 0.1
10	2.1	1.11	52	< 0.1
1000	2.3	1.20	57	< 0.1
10000	4.8	1.21	46	< 0.1
40000	4.1	1.05	27	< 0.1

other three dimensional electrodes [12]. Moreover, the power requirement and energy consumption for the laboratory cell were low and these figures of merit would be expected to improve further with scale up of the technology.

Later papers will consider the use of reticulated carbon cathodes for the removal of other metal ions, the treatment of solutions with mixtures of metal ions, the influence of stronger complexing agents and the processing of neutral and basic solutions. The per-

formance of these reticulated electrodes will be quantitatively compared to that of other three dimensional cathode structures.

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