Electrolytic recovery of metals from waste waters with the 'Swiss-roll' cell

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The 'Swiss-roll' cell has been used for the removal of copper from dilute synthetic waste waters. Batch experiments have shown that in acidic solutions the copper concentration may be taken down to a concentration under 1 ppm. Without N_2-sparging the current efficiency at a concentration of 22 ppm Cu was 30%. The cell was also used to separate metals from mixtures found in pickling baths. Thus 99·9% copper was removed from a Cu/Zn sulphate solution with no detectable change in the Zn concentration. The deposited metal may be leached out chemically or stripped out by anodic polarization.

List of symbols

a	specific cell cost ($\$ \, m^{-2} s^{-1}$)
A	electrode area (m^2)
b	integration constant (M)
c	concentration (M)
c_0	initial concentration (M)
c_∞	steady state concentration (M)
d	thickness of cathode spacer (m)
d_h	hydraulic diameter (m)
D	diffusion coefficient ($m^2 s^{-1}$)
f	friction factor
k	mass transfer coefficient ($m \, s^{-1}$)
K	flow rate independent cost per unit time ($\$ \, s^{-1}$)
K_{cell}	cost associated with cell per unit time ($\$ \, s^{-1}$)
K_{pump}	cost associated with pumping per unit time ($\$ \, s^{-1}$)
K_{tot}	total cost per unit time ($\$ \, s^{-1}$)
l	breadth of electrode perpendicular to flow (m)
L	length flow path across electrode (m)
p	specific pumping cost [$\$ \, (W \, s)^{-1}$]
ΔP	pressure drop across cell ($N \, m^{-2}$)
(Re)	Reynolds number
(Sc)	Schmidt number
(Sh)	Sherwood number
t	time (s)
v	electrolyte flow velocity ($m \, s^{-1}$)
V	volume of electrolyte in batch experiment (m^3)
Y	effluent through-put ($m^3 \, s^{-1}$)
Z	volume flow rate through cell ($m^3 \, s^{-1}$)
ϵ	porosity of cathode spacer

1. Introduction

Many of the metals that occur in industrial waste waters are poisonous and must therefore be removed before being discharged into the environment. A common method has been simply precipitation as an hydroxide by adding lime. Although the method is inexpensive, a disadvantage is, that the sludge obtained is of little value even though it may contain valuable metals. The dwindling world reserves of metals makes it most desirable to recover them from waste waters in a form that may be reused by industry. Electrolysis is one method of achieving this goal.

Some examples of waste waters are given in Table 1. The concentrations of the metal in the waste and that tolerated in surface water are very low by normal electrolysis standards. The electrolytic method is therefore faced with the problem of achieving a high rate of mass transfer even at the very low concentrations involved and secondly in often having to treat very large quantities of

Table 1.

Metal	Source	Typical concentration (ppm)	Tolerated concentration in Switzerland* (ppm)
Fe^{2+}	Coal mines	100–500	20
Cr (VI)	Electroplating	140	0·5
Cu^{2+}	Electroplating	20–120	1
Ag^+	Photographic fixers	$0·1 \, g \, 1^{-1}$	0·1
Hg^{2+}	Chlorine production	2·5–10	0·01

* Verordnung über Abwassereinleitung, Bern, 8 December 1975.

waste; for example in the automobile industry in the USA the chromium plating plants generate $1\,000\,000 \, gal \, day^{-1}$ of waste water from the rinse baths.

Modern electrochemical engineering has made considerable progress toward overcoming these problems by improving the stirring and by increasing the ratio of electrode area to cell volume. Examples that have received some attention recently are packed beds that have been used for copper [1, 2] and antimony [3] recovery or for the oxidation of ferrous ions to ferric ion [4–6], and fluidized beds for copper recovery [7]. In our laboratory the 'Swiss-roll' cell [8, 9] is being studied for both synthesis and waste water treatment. A similar design has recently been reported by du Pont [10]. We present here a preliminary report on its application to the recovery of metals from synthetic waste waters. The following experiments refer to the case of copper.

2. Equipment

The 'Swiss-roll' cell was constructed from an electrode sandwich which is shown in Fig. 1. The cathode was a titanium sheet of dimensions 15 cm x 0·013 cm x 80 cm that had been previously etched in HCl so as to provide a rough surface on which the copper deposit adhered well. The anode

was a titanium sheet with a RuO_2 coating prepared by thermal decomposition of $RuCl_3$ in air. Since the cell was to be used for metal deposition an anion exchange membrane (IONAC MA 3148) was placed between the electrodes so as to prevent the growth of metal right across the gap to the counter electrode. Because of the anion-exchange
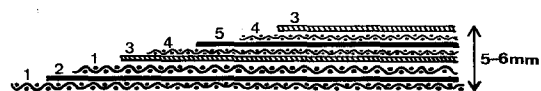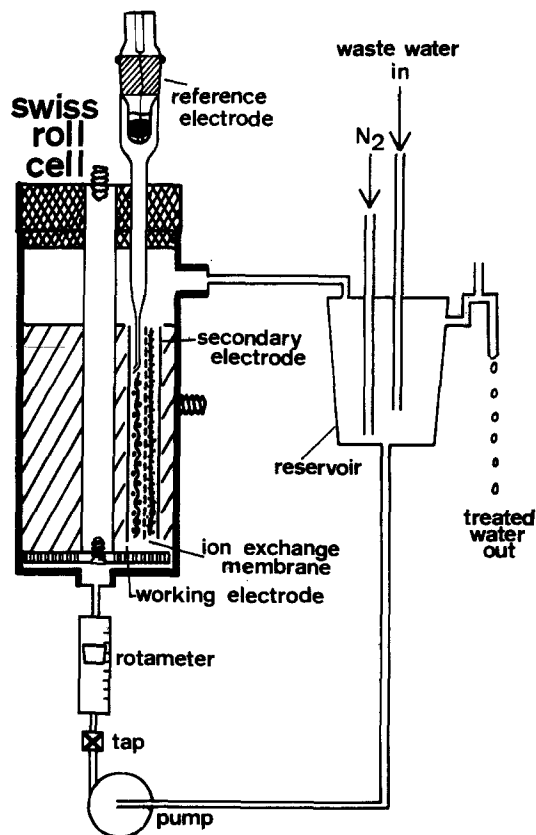

Fig. 1. 'Swiss-roll' sandwich used for deposition of copper (1) cathode separator (P1680 cloth) (2) cathode (3) ion-exchange membrane (MA 3148) (4) anode separator (P 250 cloth) (5) anode.

Fig. 2. Cross-section of 'Swiss-roll' cell and ancillary equipment.

Table 2. Cloth characteristics

Type	Mesh opening (μm)	Thread thickness (μm)	Mesh count (cm⁻¹)
P 1680	1680	800	4·03
P 250	250	200	22·2

membrane four cloth separators were required to give a volume for the electrolyte.

For the cathode space a polypropylene P 1680 cloth was taken. This having a thickness of 1·6 mm and porosity of 0·74 provided a relatively large volume for the metal being deposited. The cloth separator for the anode space was much thinner so as to maximize the specific electrode area; it also restricted the flow of electrolyte past the anode. It was a polypropylene cloth type P250 with a thickness of 0·4 mm. The cloth characteristics are shown in Table 2. At one position on the P1680 cloth a slot was cut out so as to provide a space for a luggin capillary (polythene tube) which provides a means for potential measurement. The sandwich was rolled up around a titanium axis and inserted in a PVC tube. A cross-section of the rolled up construction is shown in Fig. 2. The luggin capillary is shown and also its connection to the external reference electrode which enabled potentiostatic operation of the cell. The cell axis acted as current feeder to the anode while a bolt through the PVC container pressed against the cathode acted as the cathode current feeder. The effective cathode area was 750 cm².

All concentrations were measured by differential pulse polarography with a PAR 174 instrument.

3. Theory

We assume that the metal is deposited at the limiting current which is the maximum attainable.

3.1. Batch operation

Assume that a charge of $V(\mathrm{m}^3)$ is continuously pumped through the cell. The concentration change with time may be expressed by:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -\frac{kAc}{V} \tag{1}$$

where k is the mass transfer coefficient $(\mathrm{m\ s^{-1}})$, A the electrode area $(\mathrm{m^2})$ and c the concentration $(\mathrm{kM\ m^{-3}})$. Integrating, the instantaneous concentration is obtained:

$$c = c_0\,\mathrm{e}^{-kAt/V} \tag{2}$$

where c_0 is the initial concentration.

3.2. Continuous operation

Waste at a concentration c_0 is continuously introduced at a rate $Y(\mathrm{m^3\,s^{-1}})$ into the well-mixed circulated volume $V(\mathrm{m^3})$. The concentration of the metal in the circulated solution and also that of the 'treated' water overflowing out is $c(\mathrm{kM\ m^{-3}})$. In the system studied the conversion per pass through the cell is very small and we have therefore a system analogous to a continuous stirred tank reactor (CSTR). The mass balance is written as:

kM entering s⁻¹ = Yc_0

kM leaving s⁻¹ = Yc

kM deposited s⁻¹ = kAc

The rate of change of concentration is therefore

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{Yc_0}{V} - c\left[\frac{Y + kA}{V}\right]. \tag{3}$$

Thus

$$c = b\,\mathrm{e}^{-(Y+kA)t/V} + \frac{Yc_0}{Y + kA} \tag{4}$$

where b is an integration constant.

The starting behaviour from initial concentration c_0 is therefore given by:

$$c = c_0\,\frac{kA}{Y + kA}\,\mathrm{e}^{-(Y+kA)t/V} + \frac{Yc_0}{Y + kA} \tag{5}$$

and the steady-state concentration at large t

$$c_\infty = \frac{Yc_0}{Y + kA}. \tag{6}$$

The transient behaviour on interrupting the feed $(Y = 0)$ to the system at the steady state is then
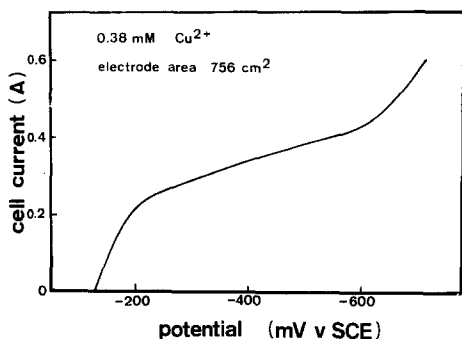
$$c = \frac{Yc_0}{Y + kA}\,\mathrm{e}^{-kAt/V}. \tag{7}$$

Fig. 3. Polarization curve obtained for the solution $CuSO_4$ $3·8 \times 10^{-4}$ M + $6·10^{-3}$ M H_2SO_4 with 'Swiss-roll' cell of electrode area $0·075$ m^2.

4. Experimental

4.1. Deposition

All solutions were made up from the sulphate salts of the metal. The current/potential characteristics of a deoxygenated $3·8 \times 10^{-4}$ M $CuSO_4$ in 6×10^{-3} M H_2SO_4 solution is shown in Fig. 3. A fairly well-defined plateau was obtained for the deposition of copper at the limiting current. In order to achieve high mass transfer rates the deposition of copper was done at $-$ 300 mV versus SCE which is in this plateau region. The variation of limiting current with flow rate is of importance in optimizing the process. The results obtained with this 'Swiss-roll' cell over a range of flow rates $1·3 \times 10^{-5}$ m^3 s^{-1} to $7·0 \times 10^{-5}$ m^3 s^{-1} are shown in Fig. 4. The experimental points are approximately represented by the following expression for the mass transfer coefficient k:

$$k = 2·79 \times 10^{-4} v^{0·71} \quad \text{(SI units)} \quad (8)$$

where v is the linear velocity of electrolyte past the cathode; it is related to the volumetric flow rate by Equation 14.

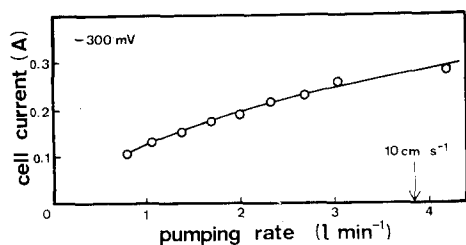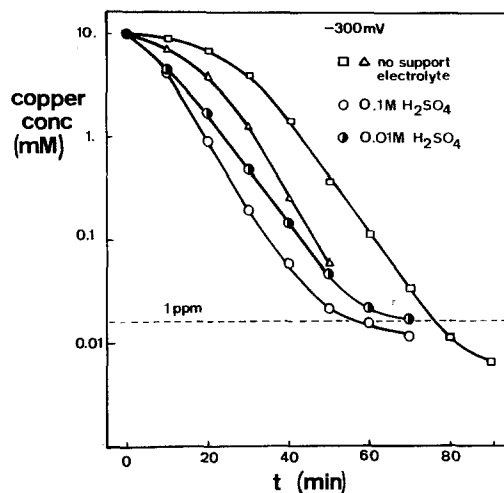As a test of the applicability of the 'Swiss-roll'

Fig. 5. Removal of copper in batch operating mode.

cell for the removal of copper from waste waters, batch experiments were first carried out. Fig. 5 shows the decrease of copper concentration with time for electrolysis at $-$ 300 mV and 1 litre of continuously recycled solution at a flow rate of $0·07$ m s^{-1}. Starting from an initial concentration of 10^{-2} M copper an end concentration of less than 10^{-5} M was obtained both in the presence of and without added H_2SO_4 as support electrolyte. Reduction to concentrations much below 10^{-5} M does not seem to be possible in these acidic solutions probably because chemical dissolution occurs at the same rate as the electrodeposition. However, the end concentration was lower than that tolerated for wastes. This electrolysis therefore meets the required waste water standard. The rather slow rate of removal of copper initially for solutions without added electrolyte could be due to diffusion control by the sulphate ions at the membrane. Equation 2 predicts for a flow rate $0·07$ m s^{-1} a factor 15 for the decrease in concen-

Fig. 4. Variation of cell current with electrolyte flow rate. With the same condtions as for Fig. 3.
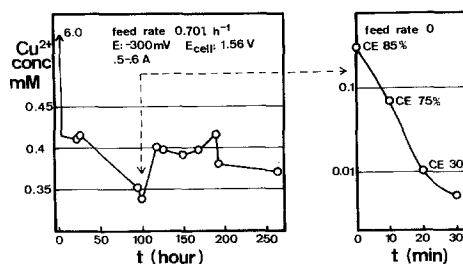

Fig. 6. Copper concentration in continuous experiment. Left: steady state, right: transient.
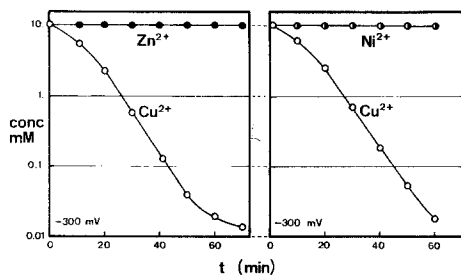
Fig. 7. Removal of copper from metal mixtures. Left: Cu/Zn, right: Cu/Ni.

tration every 10 min. That observed was about 8.

The 'Swiss-roll' cell has also been operated continuously. In these experiments 6.10^{-3} M copper sulphate solution was fed at a rate of $1.94 \times 10^{-7} m^3 s^{-1}$ (0·71 h^{-1}) to $1.2 \times 10^{-3} m^3$ (1·2 l) of solution continuously pumped through the cell at 4.48×10^{-5} m^3 s^{-1}. The treated solution left the overflow after a residence time of about 1·7 h and its concentration was measured periodically. Fig. 6 shows the effluent concentration variation over a period of 11 days during which 70 g of copper was deposited. There are small fluctuations which might arise from inaccuracies in the control of the feed rate, but on the whole the effluent concentration may be regarded as stationary, being between 3.5×10^{-4} M and 4×10^{-4} M. The cell voltage was 1·56 V and the current 0·5–0·6 A, corresponding to a current efficiency of about 30%. This low efficiency is probably due to the fact that no precautions were taken to remove the oxygen produced at the anode. Indeed, in the absence of oxygen a much higher current efficiency was observed. This is seen on the diagram to the right of Fig. 6 which shows the decrease of the copper concentration in the cell when the feed was interrupted for half an hour and oxygen was removed by nitrogen purging. The current efficiency was initially 85% (concentration 3 10^{-4} M) and even at 10^{-5} M was still 30%.

An advantage of the electrochemical treatment of waste-waters is the ability to remove a particular metal selectively from a mixture. For example, pickling baths for brasses would contain copper together with zinc. Figs. 7a and 7b show that with the 'Swiss-roll' cell copper may be successfully recovered from copper/zinc and copper/nickel mixtures. In these batch experiments the solution

initially contained the two metals at a concentration of 10^{-2} M together with 10^{-2} M H_2SO_4. 99·9% of the copper was recovered with no detectable change in the concentration of the second metal.

4.2. Stripping

The deposition of metal cannot proceed indefinitely. The space available in the reactor is limited and the metal must therefore be removed periodically before the flow channel is completely blocked. With the P1680 cloth separator theoretically 2 g copper could be deposited per cm^2 electrode area. In practice much less copper would be deposited because deposition of a powder at the limiting current is preferred. Much higher deposition rates may then be achieved.

There are three possible stripping methods:
(a) Opening up the cell and mechanically removing the deposit;
(b) Chemically dissolving out the deposit with an oxidizing acid e.g. HNO_3 or H_2SO_4/H_2O_2; or
(c) Electrochemically stripping out the deposit anodically.

All three have been tried. The first, however, would probably not be practicable for a full size cell. Chemical dissolution is a fast, convenient and inexpensive solution and is probably the preferred one. Care must be taken, however, to ensure that the electrodes are not damaged.

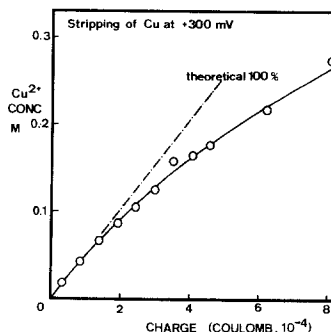Anodic stripping* can be performed with relatively mild conditions. At + 300 mV in 1 M

Fig. 8. Anodic stripping of copper deposit. Plot of copper concentration against charge consumed.

* The use of a Ti/RuO_2 auxiliary electrode is not to be recommended owing to reduction of the RuO_2. A better choice might be a carbon felt or paper (SIGRAFLEX).

H_2SO_4 the dissolution is not diffusion-controlled and therefore a very low pumping rate may be used to produce a concentrated $CuSO_4$ solution in a single pass. Alternatively the electrolyte (1 M H_2SO_4) may be continuously recycled through the cell. By selection of a suitably fine cloth separator for the counter electrode space, the flow of $CuSO_4$ solution may be greatly restricted so as to minimize the amount of copper redeposited. In Fig. 8 the concentration of copper in 1 litre (1 M H_2SO_4) continuously pumped through the cell is plotted against charge consumed (cell current 10 A). The dotted line is for 100% current efficiency. It can be seen that up to 0·1 M $CuSO_4$ the production of $CuSO_4$ proceeded at almost theoretical current efficiency, showing that the redeposition of copper was minimal.

5. Cost estimate*

The 'Swiss-roll' cell is operated in two stages: firstly metal deposition and secondly stripping of the recovered metal off-stream. During the continuous experiments with the laboratory size cell, the deposition current was 0·25 mA, while that for the stripping was 10 A. The stripping therefore takes place in a much shorter time than the on-stream deposition. This was also true for chemical stripping. Assuming 100% current efficiency the on-stream factor of the cell was 0·975, which is very close to unity. We assume therefore that the investment associated with the stripping is negligible in comparison to that for deposition. The investment cost will therefore be dictated by the deposition requirements. We shall make the cost estimate for an automated batch process treating 10 m^3 effluent per day requiring only minimal attention of 1/2 man-h week^{-1}. The total cost K_{tot} per unit time ($ s^{-1}) may be expressed as:

$$K_{tot} = K_{cell} + K_{pump} + K. \qquad (9)$$

K_{cell} and K_{pump} are the costs associated with the cell and pump, respectively, and are functions of the electrolyte flow velocity. K is a constant for a particular plant capacity and includes the costs of the control equipment, valves, piping, tanks, electrolysis power supply, chemicals and labour. As in previous publications [12] we may optimize

the process with respect to electrolyte flow velocity as follows.

The required electrode area for batch treatment of Y m^3 s^{-1} and input and output concentrations c_0 and c is obtained from Equation 2 by replacing V/t by Y

$$A = (Y/k) \ln (c_0/c) \qquad (10)$$

For k we use a general correlation that has been determined in our laboratory by Schwager [13]. It is applicable to all the cloth separators we have used:

$$(Sh) = 0·15(Re)^{0·82}(Sc)^{0·33} \qquad 5 < (Re) < 80$$
$$(Sh) = 1·27(Re)^{0·34}(Sc)^{0·33} \qquad 80 < (Re) < 1000 \qquad (11)$$

where $(Sh) = kd_h/D$; $(Re) = vd_h/\nu$; $(Sc) = \nu/D$ and ν is the kinematic viscosity.
Now K_{cell} is proportional to A and we may substitute the appropriate value of k from Equation 11 to obtain K_{cell} as a function of v:

$$K_{cell} = (aY/k) \ln (c_0/c). \qquad (12)$$

where a is the specific cell cost per unit electrode area and time ($ m^{-2} s^{-1}).

The term K_{pump} includes the purchasing price of the electrolyte circulation pump and its energy consumption. Both are more or less directly proportional to the energy imparted on the electrolyte in order to obtain the desired flow rate v.
Thus

$$K_{pump} = pZ\Delta P \qquad (13)$$

where $Z\Delta P$ (W) is the power imparted to the electrolyte, ΔP being the pressure drop across the cell (N m^{-2}) and Z the volumetric flow rate of electrolyte (m^3 s^{-1}). The constant p is the specific pumping cost [$ (W s)$^{-1}$] and includes the efficiency of the pumping as well as the unit cost of the pump.

The pressure drop may be expressed in terms of the friction factor f that has been determined by Schwager [13]:

$$f = 75 \cdot /(Re) + 0·145 = \frac{d_h}{2\rho v^2} \frac{\Delta P}{L} \qquad (14)$$

where ρ is the density of the electrolyte. Now the volumetric flow rate Z is

$$Z = ld\epsilon v. \qquad (15)$$

Thus

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* A detailed account will be given in publication [11].

Table 3. Costing for a 10 m³ day⁻¹ automated batch plant with input and output concentrations of 100 and 1 ppm respectively

	Cost ($)	Cost/unit volume (10 years 6%) ($ m⁻³)
Cell (electrode area $7 \cdot 0$ m²)	6008	$0 \cdot 22$
Power supply (170 A)	800	$0 \cdot 03$
Ancillary equipment (pump, valves, control, tanks, installation)	4441	$0 \cdot 17$
Electric power: pump	146 year⁻¹	$0 \cdot 04$
electrolysis	31 year⁻¹	$0 \cdot 01$
Labour (1/2 man-h week⁻¹)	260 year⁻¹	$0 \cdot 07$
Leaching chemicals (915 kg HNO₃)	120 year⁻¹	$0 \cdot 03$
Total		$0 \cdot 57$

Capital cost 1125 $ m⁻³ day⁻¹
Running cost $0 \cdot 15$ $ m⁻³

$$Z\Delta P = A d e v^3 (75 \cdot /(Re) + 0 \cdot 145) 2\rho/d_h \quad (16)$$

from which K_{pump} may be obtained by substitution of Equations 10 and 13.

The constant term K includes tanks, valves, pump, control equipment, power-supply, installation and labour. The individual values are shown in Table 3. The specific cell cost* a is calculated on the basis of titanium sheet at 46 $m⁻², cloth separators at 27 $ m⁻² and ion exchange membrane at 27 $ m⁻² amortized over a period of 10 years with 6% interest rate. The anodes were coated with 15 g m⁻² RuO_2 at a cost of 203 $ m⁻² amortized over 3 years. Increasing the cost by about 15% to cover construction gives a specific cell cost of $3 \cdot 7 \times 10^{-6}$ $ m⁻² s⁻¹.

The specific pumping cost P is given predominantly by the cost of electricity consumed [$0 \cdot 02$ $ (kW h)⁻¹] for unit power imparted to the electrolyte (pump/motor efficiency 70%). It was

taken to be $0 \cdot 029$ $ (kWh)⁻¹ or $8 \cdot 1 \times 10^{-8}$ $ (W s)⁻¹.

The optimum flow rate and the minimum cost may be obtained by differentiating K_{tot} with respect to flow rate and equating to zero. We have performed this calculation for several different cloth separators. The lowest costs are obtained when the thinnest separators are employed. For a cloth type T1000 (thickness $0 \cdot 76$ mm) the optimum flow rate is $0 \cdot 41$ m s⁻¹. At this flow rate the effluent processing cost for a plant of capacity 10 m³ day⁻¹ was $0 \cdot 57$ $ m⁻³ for $c_0/c = 100$. A breakdown of the costs is shown in Table 3. For the relatively small plant considered here, the cost of ancillary equipment and labour plays a dominating role. If the plant were to be scaled up considerably these two would become relatively unimportant and the effluent processing cost would approach $0 \cdot 33$ $ m⁻³. It would also be possible to lower the cell cost substancially by using cheaper electrodes (e.g. steel) or by minimizing the area of the Ti/RuO_2 electrodes with expanded or perforated metal substrates. The cost presented here should therefore be regarded as the maximum anticipated.

Until now only the debit side has been considered. The copper recovered has considerable value. For waste waters with 100–500 ppm copper content the value of $0 \cdot 13$–$0 \cdot 66$ $ m⁻³ has been quoted [14]. Thus at a concentration of about 350 ppm copper we would expect the plant to

* The calculation here is based on the cell used in these studies having a Ti/RuO_2 auxillary electrode. It presupposes that this electrode has sufficient corrosion resistance to withstand the repeated chemical leaching step (it might be possible to decrease corrosion or change of electrochemical properties by suitable polarization). In any case, the electrode is fairly costly and there exist alternatives e.g. carbon materials such as SIGRAFLEX which would be no more expensive. An investigation of the stability of anodes for the conditions of the various stripping procedures is in progress in our laboratory.

break even, the value of the recovered copper being equal to the operating costs. The running cost of the electrochemical method discussed here is the same as for the ion exchange technique; the capital cost is somewhat higher due to the expense of ancillary equipment in relation to the cell itself. For a larger plant ion-exchange technology would seem to give no cost benefit. Electrolysis with the 'Swiss roll' cell is therefore to be preferred owing to the purity of the metal obtained and the ease of performing separation of metals.

6. Conclusions

The 'Swiss-roll' cell has been shown to be an effective means for recovering copper from waste waters down to a concentration under 1 ppm. Moreover it may be used for the separation of metals and has therefore applications in the treatment of pickling baths, e.g. those for brasses. The overall processing cost for a large plant has been estimated to be about $0.33\$ \text{ m}^{-3}$ effluent, which makes it competitive with other waste treatment technologies, e.g. ion-exchange.

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