

A flow-by packed-bed electrode for removal of metal ions from waste waters

DANIEL SIMONSSON*

Swedish National Development Company, Box 34, S-184 00 Åkersberga, Sweden

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The design and performance of a full-scale, particulate flow-by electrode is described. The mass transfer rate in the electrode is high and can be estimated for different operating conditions by means of the correlation

$$Sh = 1.46 Re^{0.72} Sc^{1/3}$$

The bed is effective for waste waters with a specific conductivity above 10^{-3} mho cm^{-1} . Noble metals can be electrodeposited easily, even if bound in strong complexes, while deposition of zinc from acid solutions is highly pH-dependent.

The scale-up of a packed-bed electrochemical reactor for industrial applications is achieved by using a multi-bed cell based on the filter press principle with the appropriate number of bed electrodes.

Nomenclature

a specific surface area, m^{-2}
 C concentration, kmol m^{-3}
 d thickness of electrode, m
 d_p particle diameter, m
 D diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
 F Faraday constant, $96\,487 \text{ A s mol}^{-1}$
 I applied current, A
 k_m mass transfer coefficient, m s^{-1}
 L bed height, m

q flow rate, $\text{m}^3 \text{s}^{-1}$
 Re Reynolds number, $ud_p \nu^{-1}$
 Sc Schmidt number, νD^{-1}
 Sh Sherwood number, $k_m d_p D^{-1}$
 u liquid velocity, m s^{-1}
 U cell voltage, V
 z charge of the electrodeposited metal ion
 ϵ void fraction of the bed
 ϕ_2 potential of pore electrolyte, V
 κ_{eff} effective conductivity, mho m^{-1}
 ν kinematic viscosity, $\text{m}^2 \text{s}^{-1}$

1. Introduction

Heavy metals in waste waters from e.g. plating industries and mines constitute environmental and health risks even at very low concentrations. The ideal solution to this problem would be a process which recovers and recycles both the metal and the water. The necessary bleed from such a process must contain heavy metals in only sub-ppm concentrations. A direct approach to such a process is the electrochemical deposition of the heavy metal(s) in a particulate bed electrode. This type of electrode has received considerable research attention during the last decade [1].

Generally a distinction is made between the flow-through and the flow-by concept, depending on whether the fluid flow and the electrical current are parallel or perpendicular to each other. A comparison between these two alternative cell configurations shows that at a given maximum ohmic potential drop and reactant conversion the maximum permissible flow rate in a flow-by electrode is higher than in a flow-through electrode, provided that the length-to-depth ratio is greater than 5 [2]. This condition should most certainly be fulfilled in a technical design.

Although research on fixed-bed electrodes for removal of metals has been intense during the last

* Also of the Department of Chemical Technology, The Royal Institute of Technology, S-100 44 Stockholm, Sweden.

years only a few reports on pilot-plant or full-scale cells have been published [3–6]. There is still a lack of knowledge for the successful scale-up of particulate-bed cells. For example, most of the published mass transfer correlations are valid for Reynold numbers which may be below those in a full-scale electrode. In addition, pure laboratory research has mostly employed ‘idealized’ packed beds with truly spherical particles or layers of screens, rather than the irregularly shaped particles more likely to be used in practice.

A third aspect of great practical importance is the question of deviation from ideal plug flow in the bed electrode. In small scale laboratory cells channelling can occur easily even when the bed is carefully packed with uniform particles [7, 8]. Since channelling reduces the efficiency of the bed electrode it is of vital importance whether, or under what conditions, this effect will appear in a larger, but still thin, bed.

The purpose of this paper is to report some of the results from a development project for the design of a full-scale particulate flow-by electrode. The experimental conditions have then been chosen to correspond to technical rather than scientifically cultivated conditions.

2. Design of the flow-by electrode

The design of the particulate flow-by electrode was guided by preliminary experiments with a small, laboratory-scale electrode. The performance of this electrode was satisfactory, although a certain degree of channelling could be observed. The technical demands specified for the scaled-up electrode were:

- large surface area per unit volume (small particles)
- good mass transfer properties (small particles + high flow rate)
- reasonable pressure drop (not too small particles)
- thin electrodes (to avoid ohmic limitations of the conversion efficiency)
- in order to save floor space and reduce the risks for channelling the height-to-width ratio of the electrode should be high
- leak-proof design
- easy manufacture of cell components

easy set up and dismantling of the cell
 easy scale-up of the cell by employing a stack composed of a suitable number of standardized electrodes.

The development work was carried out in two steps. In the first step, the interest was focused on the individual electrode and its design and performance. In the second step, a complete cell stack was designed and tested.

The design of the single, particulate electrode used in the experiments is shown in Fig. 1. The bed material comprised graphite grains of varying sieve fractions. The current collectors were made of titanium and graphite. The frames of the prototype version were made in Plexiglass in order to allow visual observation of the bed. The electrode bed was surrounded by anion-selective membranes (Asahi Glass, Selemion ASV or AMV) on both sides. In the multibed stack it was also found necessary to embed the membrane between plastic nets to prevent puncture, Fig. 2.

The cell was sealed by rubber gaskets between the electrode frames.

3. Experimental procedure

The performance of the full-scale flow-by electrode was evaluated in an experimental programme with the experimental set-up shown in Fig. 3. Lead

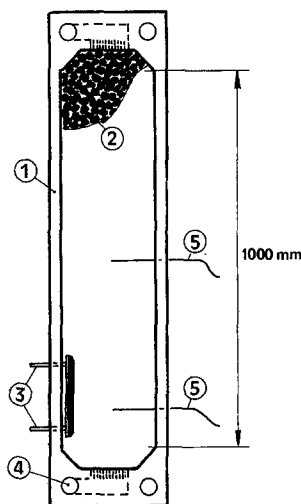


Fig. 1. Design of the particulate flow-by electrode: 1. electrode frame; 2. bed with granular carbon; 3. current feeder of titanium and graphite; 4. catholyte inlet; 5. plastic capillary tubes.

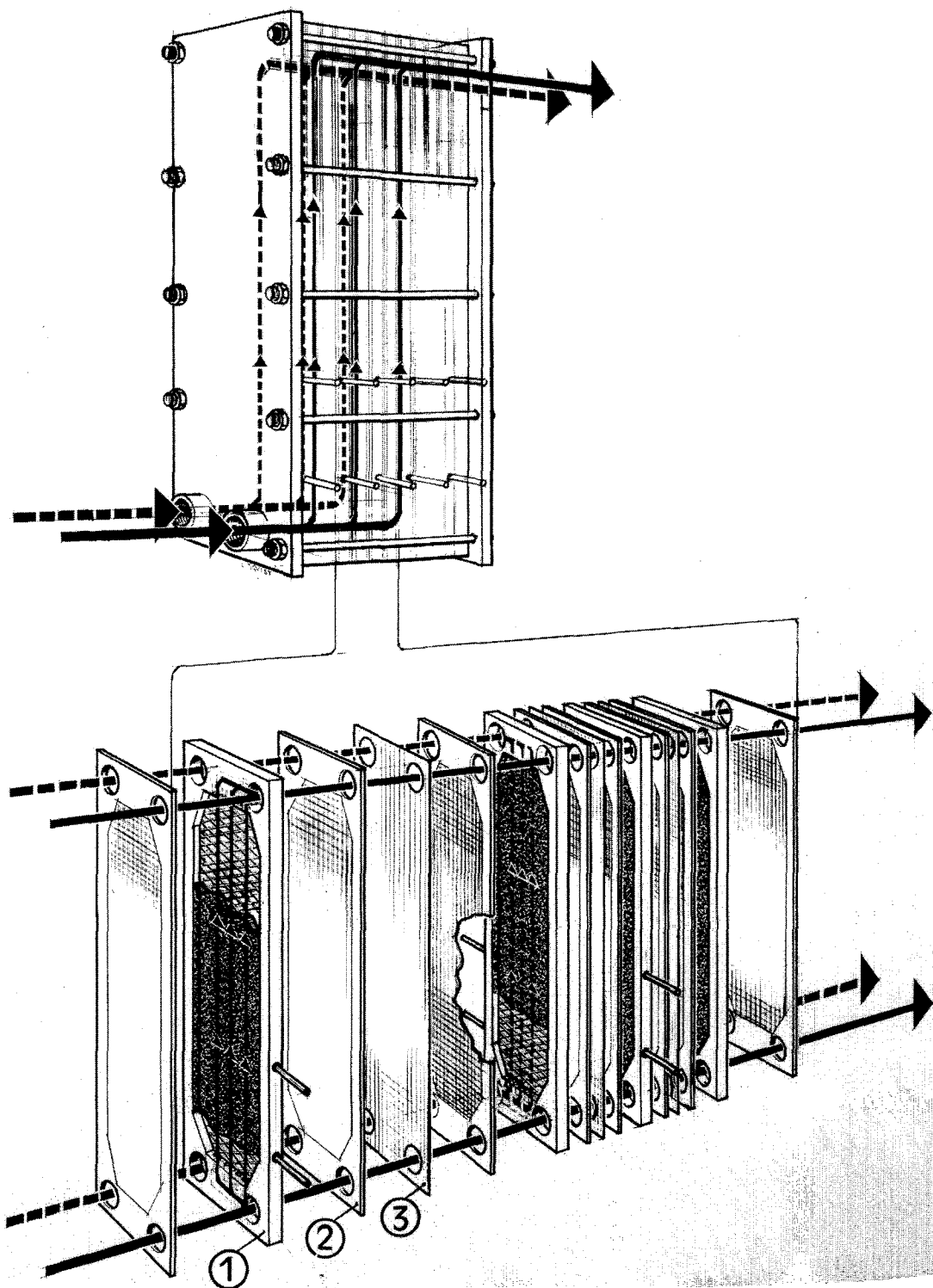


Fig. 2. Design of the multi-bed system: 1. electrode frame with bed electrode; 2. rubber gasket with plastic separator; 3. anion-selective membrane. (The figure shows an alternative design of the current collector, expanded titanium grid. The experiments reported in this article were performed with current collectors of the type shown in Fig. 1.)

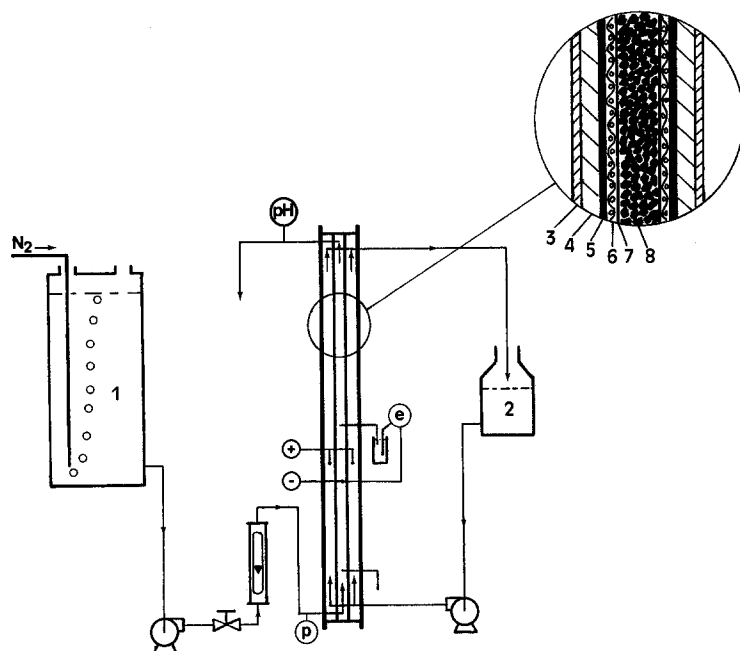


Fig. 3. Schematic flow-sheet of the experimental set-up:
 1. catholyte reservoir; 2. anolyte reservoir; 3. backing plate;
 4. Plexiglass; 5. lead anode;
 6. polypropylene net (1 mm);
 7. anion-selective membrane;
 8. bed electrode (cathode).

sheets were used as symmetrical counter electrodes. These were separated from the membranes (Asahi Glass, Selemion ASV) by polypropylene nets. The flow-by electrode was packed with graphite particles of different sizes and origins. Waste carbon from Union Carbide (UCAR) and carbonizers from HAGRAF, Sweden and Desulco, USA were used. The graphite grains for carburizing could be obtained in a size range which gave higher yields after sieving into useful fractions. The bed voidage was measured by the difference in weight between a bed of known volume filled with water and that from which water had been removed by draining and rolling the particles in damp cloths. The final bed porosity of the particulate packed bed electrode was calculated by subtracting from the initial void volume the difference in volume between the loosely packed bed and the compacted bed. The thickness of the compacted bed was 10.8 mm. Plastic capillaries were inserted into the bed at heights of 0.11 and 0.50 m, respectively. These capillaries could both be connected to a reference electrode (Cd/CdSO_4 , $0.1 \text{ M K}_2\text{SO}_4$) as well as be used to take electrolyte samples from the bed.

The anolyte was a recirculated $0.5 \text{ M K}_2\text{SO}_4$ -solution which gradually became more acidic due to the oxygen evolution reaction at the anodes. The solution was replaced by a fresh solution when

the pH decreased to below one. The catholyte was a test solution containing, in the standard case, approximately $0.5 \times 10^{-3} \text{ M CuSO}_4$ (around 30 mg Cu l^{-1}) in a $0.5 \text{ M K}_2\text{SO}_4$ -solution. The pH varied between 1 and 3 in the different runs. The flow rate of the catholyte was recorded by a calibrated rotameter. Depending on the flow rate of anolyte and catholyte, respectively, there was a net transport of water across the membranes. This flow, however, was very small in comparison to the catholyte flow rate ($< 1\%$). The change in flow rate from inlet to outlet was thus negligible. The pH of the outlet flow from the cathodic bed was recorded continuously and the metal concentration in the feed, the bed and the outlet flow was measured periodically with a Varian AA-275 Atomic Absorption Spectrophotometer. The total volume of catholyte was 50 dm^3 . Nitrogen was bubbled through this solution to expel dissolved oxygen and dissolved hydrogen from earlier experiments. Due to the relatively large volume this degassing was not complete. In addition many experiments were run without any nitrogen sparging to simulate real conditions.

Mass transfer limiting conditions were approached by increasing the current until a constant concentration profile in the bed was measured.

In the experimental cell used in the mass transfer studies the two counter-electrodes did not cover the diverging inlet section of the packed bed, see Fig. 1. Observation of deposited copper in the bed showed that this deposition extended to about 0.5 cm below the level of the lower edge of the counter-electrode. Since the height of the bed was measured from this level an error of about 1% was introduced.

The total metal deposition in the packed beds was very small and resulted in negligible effects on bed porosity and pressure drop.

4. Analysis of experimental data

The maximum metal deposition rate in the particulate bed electrode is obtained under mass transfer control throughout the bed. The efficiency of the electrode can, thus, best be measured by the average mass transfer coefficient (k_m) in the bed.

With mass transfer control and plug flow in the bed the relation between the concentration, C , at height L and the inlet concentration C_0 is given by

$$C/C_0 = \exp(-ak_m L/u) \quad (1)$$

The specific surface area of the bed can, as a first approximation, be estimated by the geometrical relationship for spherical particles.

$$a = \frac{6}{d_p}(1-\epsilon) \quad (2)$$

Observations in a stereo-microscope indicated that Equation 2 represents only a very rough approximation in view of the irregular form and the surface roughness of the graphite grains. The real surface area can be expected to be considerably larger.

Equations 1 and 2 can be combined to give

$$k_m = \frac{ud_p}{6(1-\epsilon)L} \ln \frac{C_0}{C} \quad (3)$$

The average mass transfer coefficient calculated with this equation was incorporated into an empirical correlation of the form

$$Sh = (\text{Constant}) Re^x Sc^y \quad (4)$$

The Schmidt Number, Sc , is approximately constant for most dilute waste waters. The value of the exponent y is therefore of less practical

interest and taken to be 1/3 in accordance with the Chilton-Colburn analogy.

5. Experimental results

The galvanodynamic approach to the mass transfer control region is illustrated in Fig. 4. In order to reach limiting current conditions throughout the bed the current had to be increased to values above 15 A in this experiment. At a current of 20 A a good log-linear fit was obtained for the three lower points in agreement with Equation 1. The exit concentration, on the other hand, is higher than the predicted value. This can be explained by the fact that the outlet concentration is very low: 0.02 mg l⁻¹ at 20 A. This was the lowest outlet concentration obtained in the whole series of experiments and was reached in only a few runs. More typically, the outlet concentration approached a limiting value of 0.06–0.08 mg l⁻¹. These outlet concentrations are orders of magnitude higher than the equilibrium values predicted from thermodynamics [9]. However, the minimum outlet concentration predicted by theory has not been attained in practice. Literature data is rare, but practical minimum outlet concentrations of around 0.06–0.07 mg l⁻¹ [4, 9] or 0.02 mg l⁻¹ at best [10] seem typical and can be regarded as a practical limit. Concentrations below 0.10 mg l⁻¹ were, therefore, not used in the evaluation of the mass transfer coefficient. Generally, the outlet concentration could thus be used in this evaluation only at high flow rates and with large particles, while the concentration measured through the capillary at the height of 0.50 m was used at low flow rates and smaller particles.

The currents in Fig. 4 can be compared to the stoichiometric demand of less than 12 A, which is the current necessary for the complete reduction of copper ions and dissolved oxygen, when the electrolyte is saturated with air. The excess current is consumed in hydrogen formation. The solubility of hydrogen [11] allows an excess current of about 10 A under the experimental conditions of Fig. 4 before gas evolution occurs.

No gassing was observed with 10 or 15 A. Gassing was observed at 20 A, but only in the upper part of the bed. Increasing the current (and the gassing) further did not change the concentration profile.

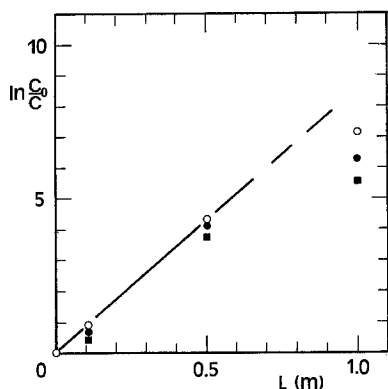


Fig. 4. Copper concentration profile along the electrode at different applied currents. Particle diameter = 1.0–1.4 mm, flow rate = 4 l min⁻¹, inlet concentration, $C_0 = 25.2$ mg l⁻¹. ■ – 10 A; ● – 15 A; ○ – 20 A.

The electrode potential in the bed electrode close to the membrane varied along the electrode due to the effect of the counter-electrode. The electrode potential measured through the lowest capillary was about or below 0.10 V against the Cd/CdSO₄ reference electrode when limiting current conditions were achieved.

Average mass transfer coefficients, calculated by means of Equation 3 for graphite particles of different sizes and origins, were transformed into

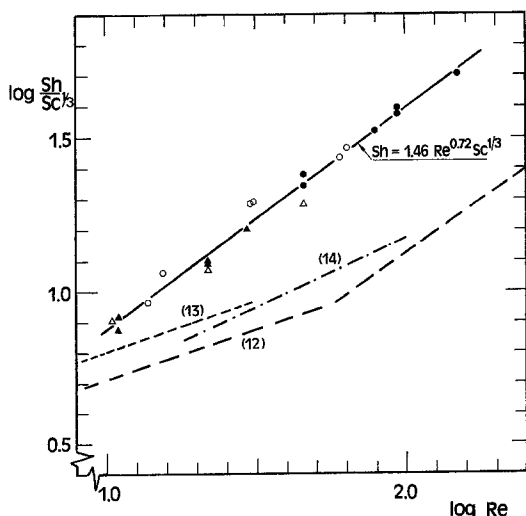


Fig. 5. Experimental mass transfer data plotted as dimensionless numbers. Comparison with some literature data for spherical particles (dashed lines). Figures in brackets are the corresponding literature references. Parameter values used are: $D = 0.6 \times 10^{-9}$ m² s⁻¹ [15, 16], $\nu = 0.98 \times 10^{-6}$ m² s⁻¹ [17], $\epsilon = 0.46$ (measured). ○ – UCAR $d_p = 1.4$ –2.0 mm; △ – UCAR $d_p = 1.0$ –1.4 mm; ● – HAGRAF $d_p = 2.0$ –3.15 mm; ▲ – HAGRAF $d_p = 1.0$ –1.4 mm.

dimensionless Sherwood numbers, which are plotted against the corresponding Reynolds numbers in a bilogarithmic diagram (Fig. 5). A straight line can be fitted to the data points by the least square method with a correlation coefficient of 0.99. For a comparison, the correlations for spherical particles according to Wilson and Geankoplis [12], Coeuret [13] and Enriquez-Granados *et al.* [14] are also given in Fig. 5. The relatively high value of the exponent of the Reynolds number indicates turbulent conditions down to relatively low Reynolds numbers. At higher Reynolds numbers the mass transfer coefficient (or Sh) is almost three times higher than would be expected for spherical particles. This indicates that the true surface area of the irregular graphite grains is about three times higher than that predicted by Equation 2 under the assumption of smooth, spherical particles.

The experimental programme also included a test on an entrance region effect. The bed was divided into two sections of 40 cm height with inert, nonconductive plastic granules in between in a 20 cm high section. The two bed sections were supplied with separate current feeders so that only one bed at a time could be used. There was no significant difference in the results when first, only the upper bed and then only the lower bed was connected to the power supply.

6. Performance under ohmic limitations

The mass transfer characteristics of the flow-by electrode were evaluated in experiments with an excess of supporting electrolyte and low inlet concentration to ensure that the limiting current density could be attained throughout the depth of the electrode without disturbances from side reactions. For this condition to be fulfilled the local electrode potential must be within a fairly narrow region of a few hundred millivolts everywhere (see, for example, Figs. 9 and 10 by Newman and Tiedemann [1]). At limiting current and with no side reactions the potential drop in the electrolyte across the depth of the bed is [4, 5]

$$\Delta\phi_2 = zFk_m C_{ad}^2 / (2\kappa_{\text{eff}}) \quad (5)$$

Using this equation, it can be estimated that in practice the application of flow-by electrodes will

Table 1. Removal of copper from electrolytes of low conductivity. Particle diameter = 1.0-1.4 mm

Input data				Results				Note		
κ_0 (10^{-3} mho cm^{-1})	C_0 ($mg\ l^{-1}$)	pH ₀	q ($l\ min^{-1}$)	I (A)	U (V)	κ_1 (10^{-3} mho cm^{-1})	κ_2 (10^{-3} mho cm^{-1})	C_1 ($mg\ l^{-1}$)	C_2 ($mg\ l^{-1}$)	a
1.06	82	2.7	2.0	12	3.54		0.51	28	1.9	
1.06	82	2.7	2.0	14	3.87	0.77	0.51	32	1.3	
1.06	82	2.7	2.0	16	3.94	0.81	0.55	33	1.4	
1.87	74	2.0	1.0	7	3.24	1.42	0.95	26	0.6	
1.87	74	2.0	1.0	7	4.22	1.48	1.06	68	56	b
1.87	74	2.0	1.0	9	4.50	1.51	1.15	70	53	
1.87	74	2.0	1.0	11	4.81	1.51	1.16	68	53	

a The electrolytes were diluted solutions of $CuSO_4$, K_2SO_4 and H_2SO_4 . Subscripts 0, 1 and 2 denote values measured at the inlet, in the middle of the bed and at the outlet, respectively. pH of the anolyte was about 11.

b Only one counter electrode was used.

Table 2. Removal of various metals from solutions of practical interest

Metal	C_0 ($mg\ l^{-1}$)	pH_0	Solution characteristics	d_p (mm)	q ($l\ min^{-1}$)	U (V)	I (A)	C_2 ($mg\ l^{-1}$)	Current efficiency (%)	Application area
Cu	67	1.4	$CuSO_4/H_2SO_4$ $\kappa = 0.030\ \Omega^{-1}\ cm^{-1}$	1.0-1.4	2.0	2.2	13	0.03	52	Rinse waters from electroplating, pickle baths
Cu	28	2.1	Complexed with quadrol $\kappa = 5.3 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$	2.0-3.15	1.0	2.3	4	0.6	35	Rinse waters from electroless plating
Zn	44.6	5	$ZnSO_4/K_2SO_4/H_2SO_4$ $\kappa = 0.019\ \Omega^{-1}\ cm^{-1}$	2.0-3.15	1.0	3.2	8	0.44	27	Acid mine waters, rinse waters from electroplating
Ag	910	3.6	[18]	2.0-3.15	1.0 (recirculation)	0.5-2.0	2	0.7	20	Fixing baths

probably be restricted to waste waters with conductivities above 10^{-3} mho cm^{-1} .

A series of experiments with electrolytes of varying conductivities was run in order to investigate the practical limit for very dilute waters. Typical results are given in Table 1. The efficiency was surprisingly good even at conductivities of only $0.5\text{--}1 \times 10^{-3}$ mho cm^{-1} in the free electrolyte. (The effective conductivity in the bed should be about 2–3 times lower.)

Table 1 also shows the strong effect of the bed depth. By connecting either both counter-electrodes or only one to the electric power supply the effective depth (d) was either 0.54 or 1.08 cm, respectively. In the latter case, the efficiency was very low. The concentration at the outlet was significantly higher than the concentration in the middle of the bed when both counter-electrodes were used. Thus, even at the same total superficial area the efficiency decreases with increasing thickness of the bed. Increasing the applied current did not help but only resulted in increased hydrogen production and a lower current efficiency.

7. Application studies

The design of the particulate-bed electrode was guided by and its mass transfer characteristics were evaluated by experiments with acidic copper sulphate solutions. The electrodeposition of copper in packed bed electrodes is favourable because of its high electrode potential. It is also of a practical interest as regards treatment of waste waters from copper electroplating baths, for example, in the printed circuit board industry. Since metal deposition in packed-bed electrodes is also of interest in other applications various tests were run on other types of waste waters. Maximum removal efficiency at a given flow rate was determined by increasing the current until the outlet concentration no longer decreased. The results are summarized in Table 2 and the different applications are commented upon below.

7.1. Complexed copper

Electroless copper plating utilizes solutions in which copper is held by strong complexing agents such as EDTA, Quadrol or Rochelle salt. Conventional treatment with hydroxide precipitation

is mostly not possible with these solutions and thus electrodeposition of the metal would be of special interest. Experiments were run with authentic solutions obtained from a printed circuit board manufacturer. These were acid-rinse water solutions containing Quadrol as a complexing agent. As can be seen in Table 2, the results indicate that the particulate flow-by electrode should be an efficient alternative in the treatment of these waste waters.

7.2. Acid zinc solutions

Waste waters containing zinc in acid solutions are generated in certain zinc electroplating processes. Electrodeposition of zinc of low concentration in acid solutions is a complicated matter due to the thermodynamics, which strongly favour the evolution of hydrogen. When acid ZnSO_4 -solutions with 0.1M K_2SO_4 were treated in the particulate-bed electrode it appeared that the pH of the anolyte strongly influenced the results: with a sulphuric acid anolyte the zinc deposition rate was very low; with an alkaline anolyte the treatment was more effective, provided that the pH of the catholyte was not too low. Fig. 6 shows the dramatic effect of lowering the pH at the inlet below 2.8. The successful treatments at higher pHs were accompanied by an increase in pH to the alkaline side. However, no simultaneous chemical precipitation of $\text{Zn}(\text{OH})_2$ could be observed. The increasing pH is caused by the simultaneous evolution of hydrogen. At a lower

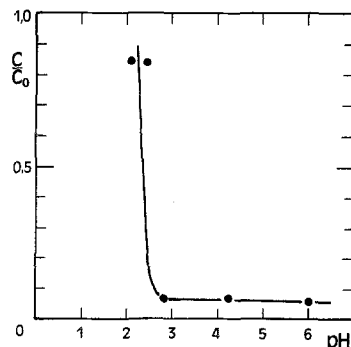


Fig. 6. Removal of zinc: dimensionless outlet concentration as a function of pH at the inlet. Particle diameter = 2.0–3.15 mm, flow rate = 1 l min^{-1} , $I = 20\text{ A}$, pH of the anolyte = 12–13, inlet concentration varied between 60 and 70 ppm.

pH of the inlet solution the applied current is not sufficient to cause a substantial increase of the pH. When dilute sulphuric acid is used as anolyte (or generated by the anodic oxygen evolution), it evidently influences the pH of the catholyte, probably by counter diffusion of HSO_4^- ions. This also hinders the increase of pH in the catholyte. The current efficiency of the zinc electro-deposition was low, around 15%. When low currents were applied the electrode potential was too high and the deposited zinc redissolved, and the zinc concentration measured at the outlet was higher than at the inlet.

7.3. Silver from photographic fixing baths

The application of fixed-bed electrodes to the recovery of precious metals such as gold or silver is of a special interest due to the very high economic value of the recovered metal. The pay-off time is therefore very short in this application.

The volumes are relatively low and the concentration relatively high, so a batchwise process with a complete recycle is to be preferred.

Solutions were prepared to simulate spent fixing baths [15]. The removal efficiency was satisfactory, as can be seen in Table 2, although the current efficiency decreased with conversion; from 45% at 200 ppm Ag to 1.4% at 1 ppm. The operating conditions were not optimized, so much better results can be expected after further process studies.

The low cell voltage is probably due to an oxidation of transferred thiosulphate ions at the anode.

8. Summary and conclusions

A full scale flow-by, particulate electrode has been designed for use in a multi-bed stack according to the filter press principle. It has proved to be efficient in the removal of heavy metals from dilute waste waters. The mass transfer rate per unit volume of the electrode bed is high and is enhanced by the surface roughness of the graphite grains. The mass transfer data obtained with this

electrode can be fitted to the correlation

$$Sh = 1.46 Re^{0.72} Sc^{1/3} \quad (10 < Re < 145) \quad (6)$$

The metal removal efficiency is satisfactory down to conductivities of around 10^{-3} mho cm^{-1} .

Possible application areas are removal of copper and zinc from rinse waters in electroplating, complexed copper from electroless copper plating and silver from photographic fixing baths.

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References

- [1] J. Newman and W. Tiedemann, *Adv. Electrochem. Electrochem. Eng.* **11** (1978) 353.
- [2] P. S. Fedkiw, *J. Electrochem. Soc.* **128** (1981) 831.
- [3] J. M. Williams and M. C. Olson, *AIChE Symposium Series* **73** (1977) 119.
- [4] G. Kreysa, *Chem. Ing. Tech.* **50** (1978) 332.
- [5] G. Kreysa and C. Reynvaan, *J. Appl. Electrochem.* **12** (1982) 241.
- [6] G. M. Cook, *Chem. Eng.* **90** (1983) 59.
- [7] R. Alkire and P. K. Ng, *J. Electrochem. Soc.* **124** (1977) 1220.
- [8] G. B. Adams, R. P. Hollandsworth and D. N. Bennion, *ibid.* **122** (1975) 1043.
- [9] J. A. Trainham and J. Newman, *J. Appl. Electrochem.* **7** (1977) 287.
- [10] G. Kreysa, *Chem. Ing. Tech.* **55** (1983) 23.
- [11] 'Handbook of Chemistry and Physics', CRC Press Inc., 60th ed. 1979-80.
- [12] E. J. Wilson and C. J. Geankoplis, *Ind. Eng. Chem. Fundam.* **5** (1966) 9.
- [13] F. Coeuret, *Electrochim. Acta* **21** (1976) 185.
- [14] M. A. Enriquez-Granados, D. Hutin and A. Storck, *ibid.* **27** (1982) 303.
- [15] D. N. Bennion and J. Newman, *J. Appl. Electrochem.* **2** (1972) 113.
- [16] P. Hannaert, *Ind. Chim. Belge* **32** (1967) 223 (cited in V. A. Ettel, B. V. Tilak and A. S. Gendron, *J. Electrochem. Soc.* **121** (1974) 867).
- [17] 'International Critical Tables of Numerical Data', Vol V, McGraw-Hill, New York (1929).
- [18] J. Van Zee and J. Newman, *J. Electrochem. Soc.* **124** (1977) 706.