

Application of the trickle tower to problems of pollution control.

I. The scavenging of metal ions

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The theory of metal deposition in a bipolar trickle tower is reviewed briefly and applied to the scavenging of copper, silver, lead and calcium from dilute streams. Measurements of reference potential and mass-transfer coefficients for the copper system in one tower allow estimates of θ_L , the fractional active length, to be made and subsequently allow data from different towers to be collapsed into a universal plot, thus substantiating the theory at least to a first approximation. In the co-deposition of copper, lead and cadmium, the data for copper and lead can be collapsed, but for cadmium cannot, probably because cadmium's reference potential is very negative under the conditions of the experiments. A scaling law is proposed which can be used in the design of practical systems.

Nomenclature

a length of one bipolar element (cm)
 c concentration (mol cm⁻³)
 c^0 initial concentration (mol cm⁻³)
 c_i inlet concentration (mol cm⁻³)
 c_o outlet concentration (mol cm⁻³)
 c_t concentration in reservoir (mol cm⁻³)
 F the Faraday (C mol⁻¹)
 h thickness of falling electrolyte film (cm)
 K mass transfer coefficient (cm s⁻¹)
 L wetted perimeter per layer of elements (cm)
 $m = F\rho Kc/h$ (V cm⁻²)
 p numbers of elements in tower
 t time (s)
 u velocity of film (cm s⁻¹)
 v_o volumetric flow rate (cm³ s⁻¹)

V inventory (cm³)
 x distance along length of element (cm)
 ϕ potential
 ρ resistivity of solution (Ω cm)
 θ_L fractional active length

Subscripts

M solid phase
 s solution phase
 i inlet
 o outlet

Superscripts

o initial
 R reversible
 T total (across one element)
 ()^o reference state

1. Introduction

The recovery of metal from process streams is economically attractive if the metal value pays for the process, so that in the case of platinum, gold and silver, and to a lesser extent nickel, cobalt and copper, plants of high capital cost may be justified. In the majority of cases, however, the stream is dilute in metal ions and the value of the recovered metal cannot service the capital invested; thus, for example, silver in photographic solution is not reduced to a very low level. In the chemical industry precipitation methods have often been used, but the precipitate may be unfilterable and legislation is hardening against landfill. The bipolar trickle tower is a very low cost electrochemical cell which has been found to be effective in dealing with process streams, providing an alternative technology.

The trickle tower has been described extensively elsewhere [1-5]. Briefly, it consists of a tower (glass or plastic) packed with layers of conducting elements (usually carbon Raschig rings, although perforated

plates, nets, rods and spheres have been used). Each layer is separated from the next by thin plastic insulating nets. The solution is sprayed into the top of the tower and falls over the packing as a thin film. An electrical potential applied across the tower (typically 1–3 V per layer of packing) induces bipolarity in each element, so that opposite ends are anodic and cathodic, with a neutral zone in between. There are $(n + 1)$ cells in series if there are n layers of packing. The current and potential distributions have been discussed elsewhere [2, 3, 5]. In the laboratory, the cell is usually run with batch recycling of the solution, but single-pass operation, as in a cartridge filter, is also possible [3, 6].

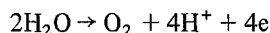
2. Theory

2.1. Active area

Metal deposition from a dilute solution in a trickle tower is essentially mass-transfer controlled [5, 7], so that for a thin Raschig ring the outlet concentration is related to the inlet concentration c_i by [5]

$$c_o = c_i \exp(-Kpa\theta_L/hu) \quad (1)$$

where θ_L is the fraction of the length, a , of a bipolar element which is active cathodically, p is the number of elements in series, h is the solution film thickness, K is the mass transfer coefficient and u the average velocity in the falling film. Since K , h and u are related to volumetric flow rate, at a fixed flow rate the only independent variables are p and θ_L , the latter being a function of applied potential. Consider Fig. 1, which is a sketch of one bipolar element (usually in our case a Raschig ring) as a zoned reactor; the length of the anodic zone is ignored, since the usual counter reaction is



and is activation controlled under the conditions of the experiments. Ohm's law applied in the inactive and active regions gives

$$\frac{d^2 \phi_s}{dx^2} = 0 \quad (2)$$

and

$$\frac{d^2 \phi_s'}{dx^2} = \frac{nF\rho Kc}{h} \quad (3)$$

from which

$$\alpha_1 x = \frac{F\rho Kc}{h} x_1^2 + \alpha_2 x_1 + \beta_2 \quad (4)$$

since $\phi_s = \phi_s'$ at $x = x_1$ and $\beta_1 = 0$ since $\phi_s = 0$ at $x = 0$, and $n = 2$ for most cases of interest. Also, since

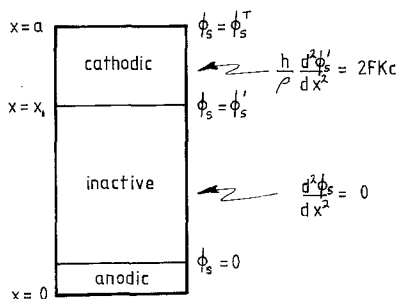


Fig. 1. Bipolar element as a zoned reactor.

$$\frac{d\phi_s}{dx} = \frac{d\phi'_s}{dx}$$

at $x = x_1$,

$$\alpha_1 = \frac{2F\rho Kc}{h} x_1 + \alpha_2. \quad (5)$$

Finally

$$\phi_s = \phi_s^T \quad \text{at } x = a,$$

therefore

$$\phi_s^T = \frac{F\rho Kca^2}{h} + \alpha_2 a + \beta_2. \quad (6)$$

Substituting Equations 5 and 6 into Equation 4

$$\alpha_1 = \frac{\phi_s^T}{a} - \frac{F\rho Kc}{ha} (a - x_1)^2. \quad (7)$$

Now, at $x = x_1$, $\phi_s = \phi_s^R = -\phi_M^R$ where ϕ_s^R and ϕ_M^R are reversible potentials of the reaction in the solution and solid phases respectively; therefore

$$\phi_s^R = \alpha_1 x_1 = \frac{\phi_s^T}{a} x_1 - \frac{F\rho Kc}{ha} x_1 (a - x_1)^2. \quad (8)$$

Rearranging Equation 8 and writing

$$\frac{F\rho Kc}{h} = m \quad (9)$$

gives

$$\frac{\phi_s^R}{m} \left(\frac{a}{x_1} \right) - \frac{\phi_s^T}{m} = -(a - x_1)^2. \quad (10)$$

This cubic equation has one negative and two positive roots, the only one in the range $0 \leq x \leq a$ being

$$x_1 = a \left[\frac{2}{3} + 2 \left(\frac{\beta}{3a^2} + \frac{1}{9} \right)^{1/2} \cos \xi \right] \quad (11)$$

where

$$\xi = \frac{1}{3} \cos^{-1} \left[\left(\frac{\beta}{3a^2} - \frac{\alpha}{2a^2} - \frac{1}{27} \right) \left(\frac{\beta}{3a^2} + \frac{1}{9} \right)^{-3/2} \right] + \frac{4\pi}{3}$$

$$\alpha = \phi_s^R/m \quad \text{and} \quad \beta = \phi_s^T/m$$

so that θ_L , the fraction of the length which is active, is given by:

$$\theta_L = 1 - \frac{x_1}{a}. \quad (12)$$

While Equations 11 and 12 give an exact value for θ_L , Equation 11 is not easy to use in further analysis [3] and it is better to proceed with a sensible approximation. Under the conditions of the experiments, as $c \rightarrow 0$

$$\frac{x_1}{a} \rightarrow \frac{\phi_s^R}{\phi_s^T}$$

while as $c \rightarrow \infty$

$$\frac{x_1}{a} \rightarrow 1.$$

The assumption is therefore made that, over the concentration range of the experiments, x_1/a only deviates slightly from the limiting value at $c = 0$, i.e.

$$\frac{x_1}{a} = \frac{\phi_s^R}{\phi_s^T} + \Delta. \quad (13)$$

Substitution of Equation 13 into Equation 10 gives

$$(\phi_s^R/\phi_s^T)^3 + 3\Delta(\phi_s^R/\phi_s^T)^2 - 2(\phi_s^R/\phi_s^T)^2 - 4\Delta(\phi_s^R/\phi_s^T) + (\phi_s^R/\phi_s^T) + \Delta - \Delta\phi_s^T/ma^2 = 0$$

higher-order terms being neglected. If Δ is sufficiently small

$$\Delta \cong ma^2 \left(\frac{\phi_s^R}{\phi_s^T} - 1 \right)^2 \frac{\phi_s^R}{(\phi_s^T)^2}. \quad (14)$$

Therefore, using Equations 12 and 13,

$$\theta_L \cong 1 - \frac{\phi_s^R}{\phi_s^T} - \frac{F\rho Kca^2}{h} \left(\frac{\phi_s^R}{\phi_s^T} - 1 \right)^2 \frac{\phi_s^R}{(\phi_s^T)^2}. \quad (15)$$

It should be remembered that

$$\phi_M^R = (\phi_M^R)^\circ + \frac{RT}{2F} \ln \frac{c}{c^0} \quad (16)$$

so that

$$\phi_s^R = (\phi_s^R)^\circ - \frac{RT}{2F} \ln \frac{c}{c^0} \quad (17)$$

where $(\phi_s^R)^\circ$ and $(\phi_s^M)^\circ$ are standard potentials with respect to oxygen evolution (the counter reaction) in the solution and solid phases respectively and c^0 is the *initial* concentration of the metal ions (the reference state). Neglecting second-order terms, Equation 15 becomes

$$\theta_L = 1 - \frac{(\phi_s^R)^\circ}{\phi_s^T} + \frac{RT}{2F\phi_s^T} \ln \frac{c}{c^0}. \quad (18)$$

2.2. Multiple-pass system: batch recycling

One of the expressions for θ_L can now be substituted in Equation 1 to obtain the outlet concentration of the reactor c_o in terms of the inlet concentration c_i . Unfortunately Equation 11 is not amenable to further manipulation, so substituting the approximate expression (Equation 18) one obtains:

$$c_o \cong c_i \exp \left\{ -\frac{Kpa}{uh} \left[1 - \frac{(\phi_s^R)^\circ}{\phi_s^T} + \frac{RT}{2F\phi_s^T} \ln \frac{c_i}{c^0} \right] \right\} \quad (19)$$

where c^0 is the original, reference concentration. Further manipulation leads to:

$$c_o = c_i \left[\frac{c_i}{c^0} \right]^{KpaRT/uh2F\phi_s^T} \exp \left\{ -\frac{Kpa}{uh} \left[1 - \frac{(\phi_s^R)^o}{\phi_s^T} \right] \right\}. \quad (20)$$

Putting in typical values of $KpaRT/uh2F\phi_s^T = O(10^{-3})$ Equation 20 approximates to

$$c_o \cong c_i \exp \left\{ -\frac{KpaL}{v_o} \left[1 - \frac{(\phi_s^R)^o}{\phi_s^T} \right] \right\} \quad (21)$$

where L is the wetted perimeter of the packing per layer and $v_o = uhL$ is the volumetric flow rate of solution through the tower. If the cell has negligible volume compared with the inventory of solution V in a well-stirred reservoir, then the mass balance equation can be written as

$$-V \frac{dc_t}{dt} \cong v_o (c_i - c_o) \quad (22)$$

and, since the concentration in the tank c_t is close to c_i ,

$$-\ln \frac{c_t}{c^0} \cong \frac{v_o}{V} \left\{ 1 - \exp \left[-\frac{KpaL}{v_o} \left(1 - \frac{(\phi_s^R)^o}{\phi_s^T} \right) \right] \right\} t. \quad (23)$$

3. Experimental

An 8 cm internal diameter QVF glass column was packed with from 20 to 56 layers of Raschig rings cut from 1.2 cm diameter Morganite graphite hollow rod. At different times rings varying from 1.0 to 2.5 cm in length were used. Adjacent layers were separated with 1 mm thick discs of Nylon mesh, and the current feeders were 5 mm plates of Morganite EY110 graphite drilled with many holes. Ceramic rings were placed on top of the upper feeder to improve fluid distribution. The fluid was sprayed into the column with a glass shower-type spray head.

Voltages of from 1 to 3 V per layer were applied, i.e., 20 to 171 V, using a Sorenson-type power supply; unless the system was driven into gas evolution the current did not exceed 0.25 A in most cases.

Experiments were run with batch recycling, the inventory of solution usually being 2 or 3 dm³ and the flow rate 1 to 3 dm³ min⁻¹. From other measurements [2, 3, 5] the average film thickness is known to be of the order of 0.05 cm under these conditions. Mass transfer and fluid distribution can be improved by co-current gas sparging, but this was not employed in these experiments, which were designed to be close to industrial practice.

Most experiments were performed with an initial concentration of 400 ppm (6.25×10^{-3} M) CuSO₄ with 3×10^{-2} M H₂SO₄ as supporting electrolyte, but runs were also made with mixtures of metals (typically 96 ppm Cu²⁺, 78 ppm Pb²⁺ and 32 ppm Cd²⁺ in 1.5×10^{-2} M HNO₃), and Ag⁺ in thiosulphate. Metal ion concentrations in samples were measured with a Varian Techtron 110 atomic absorption spectrometer.

4. Results and discussion

Figs. 2, 3 and 4 show typical results for the depletion of Cu²⁺, Cd²⁺, Pb²⁺ and Ag⁺ in various sizes of trickle tower under various conditions. As required by Equation 23 the semilogarithmic plots are all linear down to low concentrations, when the rate clearly diminishes. This can be explained by the variation of θ_L , the fractional active area, with concentration, but before θ_L can be evaluated it is necessary to obtain values of $(\phi_M^R)^o$ and K .

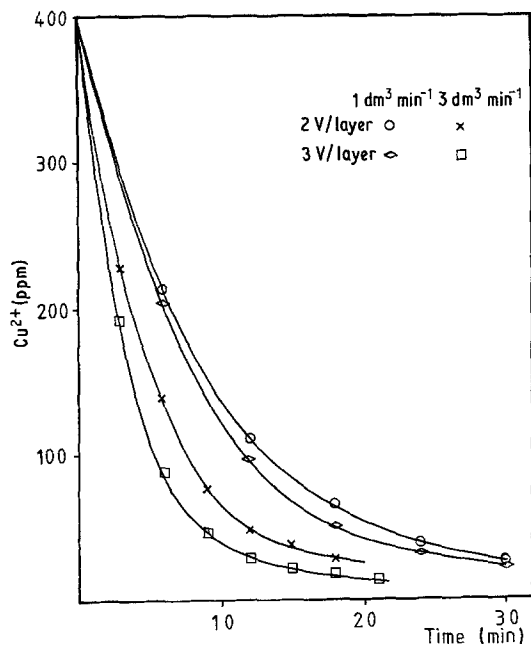


Fig. 2. Depletion of Cu^{2+} in a bipolar trickle tower; 57 layers of 1.25 cm Raschig rings.

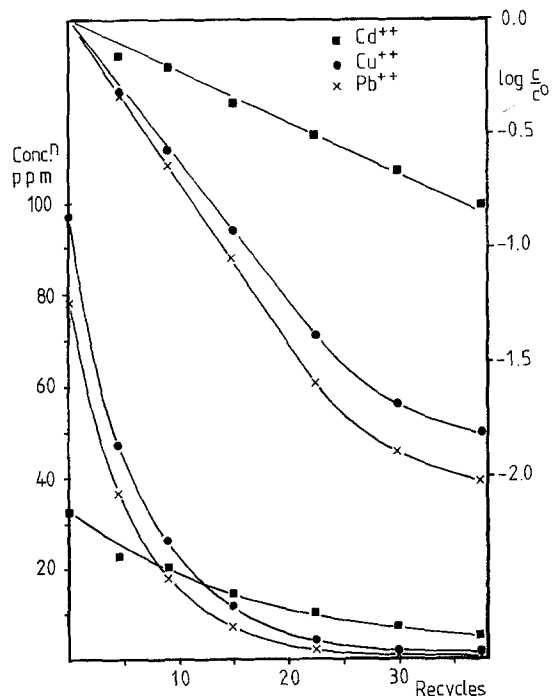


Fig. 3. Depletion of Cu^{2+} , Pb^{2+} and Cd^{2+} in nitrate solution; 29 layers of 1.25 cm Raschig rings, 3 V/layer, $3 \text{ dm}^3 \text{ min}^{-1}$.

4.1. Estimation of $(\phi_s^R)^\circ$ and K

Rearranging Equation 23

$$(\phi_s^R)^\circ = \phi_s^T + \frac{v_o \phi_s^T}{KpaL} \ln \left(1 + \frac{V}{v_o t} \ln \frac{c_i}{c^0} \right) \quad (24)$$

which can be evaluated using experimental data and assumed values of the group $(v_o/KpaL)$. Fig. 5 shows plots of $(\phi_s^R)^\circ$ versus $(v_o/KpaL)$ for three experiments run at a flow rate of $2 \text{ dm}^3 \text{ min}^{-1}$. Clearly the intersection gives the correct values of $(\phi_s^R)^\circ$ and $(v_o/KpaL)$, from which K can be calculated. Results for these and other experiments are shown in Table 1. There were insufficient data to allow this method to be used to evaluate values of $(\phi_s^R)^\circ$ for Pb^{2+} and Cd^{2+} , therefore these were estimated via the Nernst relationship, knowing the values of E^0 for the three ions.

4.2. Estimation of θ_L

The fraction of the ring length, θ_L , which is active is given exactly by Equation 11 and approximately by Equations 15 and 18. Equation 11 was solved using the estimated values of $(\phi_s^R)^\circ$ and K for the copper system and θ_L is shown as a function of concentration in Fig. 6. At low applied potentials [therefore low values of $(\phi_s^R)^\circ$] θ is almost independent of concentration down to about 50 ppm, when it decreases, which accounts for the departure from linearity in the semilog plots (Figs. 2, 3 and 4) since the net rate of deposition is the difference between the rates of deposition and dissolution from previously active areas, which may be described by an integro-differential equation [3]. Note that deposition does not stop, but the rate drops and the deposited metal redistributes itself towards the ends of the

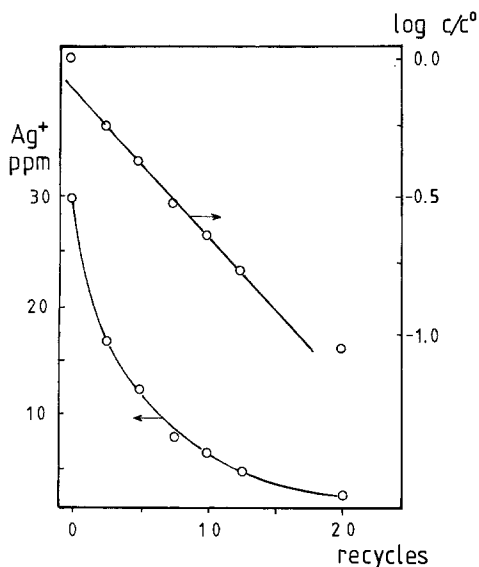


Fig. 4. Depletion of Ag^+ in thiosulphate solution; 14 layers of 1.25 cm Raschig rings, 3 V/layer, $\text{dm}^3 \text{min}^{-1}$.

elements. This must be a general phenomenon in all three-dimensional electrodes operating in batch depletion. In a single-pass system θ_L is a function of column height, but for constant input conditions it does not change with time.

At high applied potentials, θ_L at first increases before attaining a maximum; this increase probably accounts for the high initial rate seen under some conditions (Fig. 4). The maximum moves to lower concentrations as the applied potential increases. Values of θ_L from Equations 11 and 15 agree tolerably well except at the highest values of ϕ_s^T ; values from Equation 18 overestimate θ_L at high concentrations. Since this equation was used to find K , the estimated value of K is probably low; better estimates of K and θ_L could be made by iterative improvement but, in view of other uncertainties (e.g. the degree of randomness in the packing and variations in distance between layers, which affect ϕ_s^T through the iR drop), this is not worthwhile.

Measured values of θ_L in copper deposition experiments lie in the range 10–30%, depending on conditions, in reasonable agreement with prediction.

4.3. Scaling law

Despite the various approximations discussed above, Equation 23 can be used as a scaling law. For example, Fig. 7 shows a plot of $(-\ln c/c^0)$ versus the right-hand side of Equation 23 for a number of experiments run under different conditions. Agreement is satisfactory except in the case of Cd^{2+} ; how-

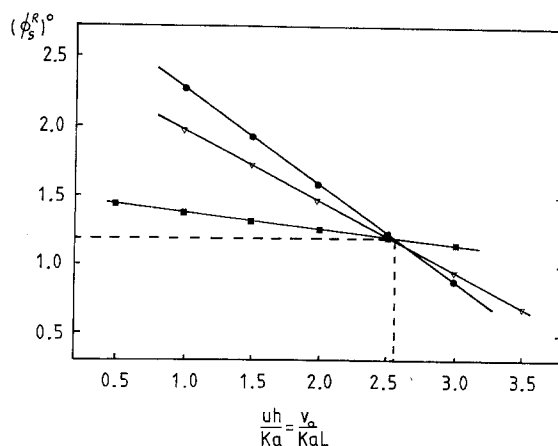


Fig. 5. Estimation of $(\phi_s^R)^0$ and K for copper deposition using Equation 24.

Table 1. Estimates of $(\phi_s^R)^0$ and K under the conditions of the experiments

System	Flow rate ($\text{dm}^3 \text{min}^{-1}$)	$(\phi_s^R)^0$ (V) [†]	K (cm s^{-1})
Cu^{2+}	1	1.21	0.00073
Cu^{2+}	2	1.20	0.0010
Cu^{2+}	3	1.20	0.0014
Pb^{2+}		1.70	
Cd^{2+}		1.98	

[†] With respect to oxygen evolution.

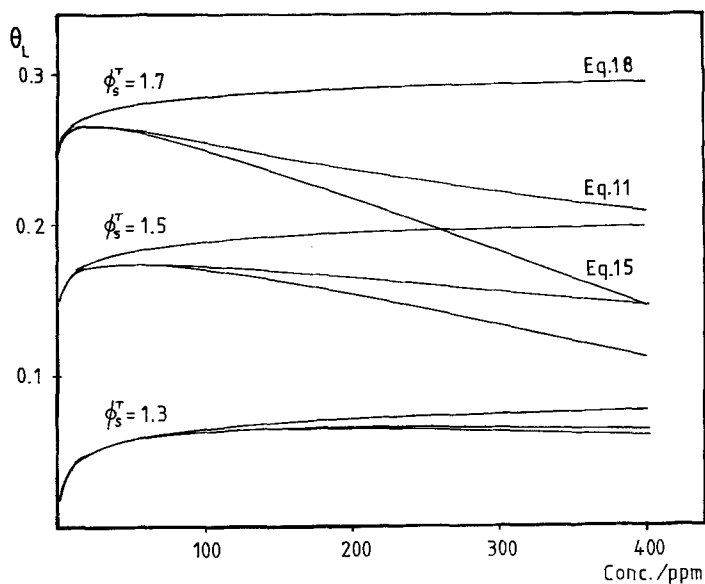


Fig. 6. Estimation of θ_L for different values of ϕ_s^T using Equations 11, 15 and 18.

ever, as Table 1 shows, $(\phi_s^R)^\circ$ for Cd^{2+} is about 2 V under the conditions of the experiment, and when due allowance has been made for the iR drop across the insulating nets the calculated value of θ_L is only of the order of 1%. In fact it is quite likely that cadmium deposition in these experiments was at least partially under activation control.

Since Equation 23 expresses the behaviour reasonably well the inference is that the rate of removal of metal is proportional to the number of layers of packing, p , the wetted perimeter per layer, L , the length of the element, a , and the applied potential. While the rate of deposition increases with flow rate, the percentage of metal extracted per pass is inversely proportional to it. Provided that the fluid is well distributed, a linear scaling law has been found in other applications of the trickle tower [2].

5. General conclusions

The bipolar trickle tower is a cheap and effective means of lowering the metal ion concentrations in pro-

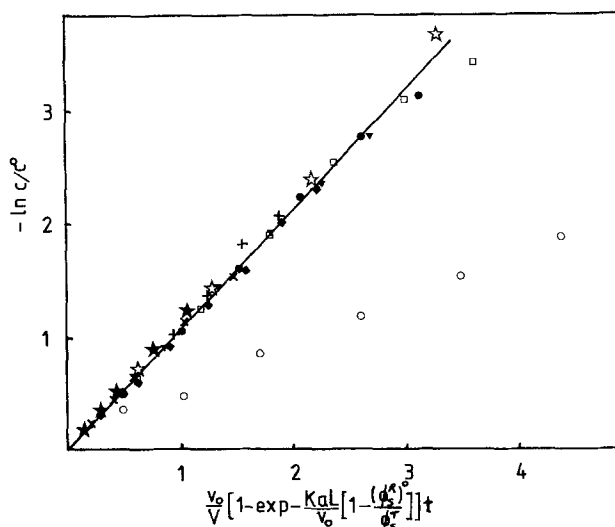


Fig. 7. Collapse of depletion data for different Cu^{2+} systems using the design equation (Equation 23).

Table 2

Symbol [†]	Number of layers	Ring length (cm)	Voltage (V/layer)	Flow rate (dm ³ min ⁻¹)
▲	43	1.25	2	1
+	20	1.25	3	3
●	57	1.25	2.5	2
○	29	2.5	3	3
☆	29	2.5	3	3
□	57	1.25	3	2
×	57	1.25	1.5	2
◆	43	1.25	2	2
★	20	1.25	2	2

[†] All results pertain to the Cu²⁺ system except ☆, which is for the Pb²⁺ system and ○, which is for the Cd²⁺ system.

cess streams to a few parts per million. In common with all three-dimensional systems, the active area decreases at very low concentrations due to the Nernstian shift in reversible potential. Therefore, if very low effluent concentrations are required, the cells are best run in cascade. Metal accumulated over a long time may be removed in one column volume of solution by backflooding and reversing the potential briefly. Mixtures of metals may be removed, but kinetic factors may then be important in some cases.

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