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Application of the trickle tower to problems of pollution control. II. The direct and indirect oxidation of cyanide

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The direct and indirect oxidation of cyanide at concentrations typical of those found in plating wash water have been investigated in a bipolar trickle-tower reactor. It has been found that the oxidation by hypochlorite generated *in situ* was faster than direct oxidation or oxidation in the presence of base, but that the CN^- concentration was easily reduced by any of these methods. Scaling-up experiments were performed by using different numbers of layers of bipoles, different electrolyte flow rates and different applied voltages. It is shown that the overall rate is determined by the mass-transport-limited generation of oxidant.

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})
F	the Faraday (C mol^{-1})
h	thickness of falling electrolyte film (cm)
K	mass transfer coefficient (cm s^{-1})
$K' = K\theta_L$	effective mass transfer coefficient (cm s^{-1})
L	wetted perimeter per layer of elements (cm)
p	numbers of elements in tower
t	time (s)
u	velocity of film (cm s^{-1})
v_o	volumetric flow rate (cm^3 s^{-1})
V	inventory (cm^3)
x	distance along length of element (cm)
ϕ	potential (V)
ρ	resistivity of solution (Ω cm)
θ_L	fractional active length

Subscripts

M	solid phase
s	solution phase

Superscripts

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

1. Introduction

Cyanide-containing effluents are obvious ecological hazards [1] and recently many countries have imposed severe regulations limiting CN^- to very low levels in running water [2]. As a consequence there is currently much interest in the destruction of cyanide in plant stream effluents, e.g. plating-bath wash water, by the most cost-effective means; often large volumes of effluent are involved with relatively low concentrations of CN^- (10 to 100 ppm). At present the most usual method of treatment is by the addition of chlorine or hypochlorite [3, 4], both of which, may be generated *in situ*, although the low CN^- concentrations may not justify the high capital cost of a sophisticated electrochemical cell. A study was therefore made of the destruction of CN^- in a bipolar trickle tower, which is a low capital cost electrochemical cell suitable for tertiary water treatment. The

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oxidation of CN^- with simultaneous co-deposition of heavy metals will be reported separately [5].

In general the bipolar trickle tower consists of a glass or plastic column packed semi-randomly with layers of graphite Raschig rings [6], although plates drilled with holes, grids or nets have also been used [7, 8]. Each layer is isolated electrically from the next by an insulating mesh of plastic. Solution is sprayed into the tower and falls as a thin film over the packing; when a voltage is applied across the tower as a whole bipolarity is induced in each layer of packing by virtue of the ohmic drop in the solution and a Faradaic reaction takes place at either end of each element. Because the volume of free space is relatively large, gas disengagement is easy; the cell may be used simultaneously as an electrochemical reactor and a sorbtion tower [9]. Note that electrogenerated species are injected at discrete locations in space so that in chemical engineering terms the cell approximates to a cross-flow reactor. Since the cell operates in the high voltage/low current regime, rather than at low voltage/high current, transformer/rectifier costs are minimal and the capital cost of associated electrical equipment is also low.

2. Reaction schemes

It has been suggested [10] that the mechanism of the direct electrochemical oxidation of cyanide is as follows:

$$CN^- \longrightarrow CN^{\cdot} + e$$
$$CN^{\cdot} + CN^{\cdot} \longrightarrow C_2N_2 \qquad (2)$$

followed by hydrolysis:

$$C_2N_2 \xrightarrow{H_2O} \left\{ \begin{array}{lll} HCN \xrightarrow{H_2O} HCOONH_4 & & (3) \\ HOCN \xrightarrow{H_2O} NH_4OCN & & \\ \xrightarrow{H_2O} CO(NH_2)_2 & & (4) \\ H_2NCCNH_2 \xrightarrow{H_2O} (NH_4)_2C_2O_4 . & & (5) \end{array} \right.$$

In the presence of hydroxide ion this scheme is modified [11]:

$$CN^- \xrightarrow{-e}$$

$$CN^{\cdot} \xrightarrow[\text{or } + CN^{\cdot}]{+ CN^- - e} C_2N_2 \xrightarrow{4H_2O} (COO)_2^{2-} + 2NH_4^+ \qquad (6)$$

(at low OH^- conc.)

$$C_2N_2 \xrightarrow{2H_2O} CN^- + CNO^- + H_2O$$

(at high OH^- conc.)

(7)

$$CN^{\cdot} \xrightarrow[-e]{+ OH^-} HOCN \xrightarrow{+ OH^-} CNO^- + H_2O \qquad (8)$$

(at high OH^- conc.)

If chloride is present under neutral conditions the formation of hypochlorite is possible according to:

$$\text{Anode:} \quad 2Cl^- \xrightarrow{1.36\,V} Cl_2 + 2e \qquad (9)$$

$$\text{Cathode:} \quad 2H_2O + 2e \xrightarrow{-0.83\,V} H_2 + 2OH^- \qquad (10)$$

$$\text{Bulk:} \quad Cl_2 + H_2O \longrightarrow HCl + HOCl \qquad (11)$$

$$HOCl \rightleftharpoons H^+ + OCl^- \qquad (12)$$

while under strongly alkaline conditions the hydrolysis is sufficiently fast for the anodic reaction to be written

$$Cl^- + 2OH^- \xrightarrow{0.90\,V} ClO^- + H_2O + 2e \qquad (13)$$

In either event the overall reaction with sodium cyanide can be written as [4]:

$$2NaCN + 5HOCl \longrightarrow 2CO_2 + N_2 + H_2O + 3HCl + 2NaCl. \qquad (14)$$

3. Experimental

Trickle towers of two sizes were used. The first was a 62 mm diameter glass column packed with seven layers of 6.5 mm x 6.5 mm Raschig rings; there were 77 rings in each layer (giving a total wetted perimeter of 242 cm per layer) and the layers were separated with 1 mm thick PVC mesh. The feeder electrodes at the top and bottom of the tower were carbon cloths (type TGH 285, Le Carbone Ltd) forming an eighth cathode/anode pair. This cell was used for exploratory studies. The second cell was a 1.2 m long QVF glass column of 75 mm internal diameter packed with 12.5 mm x 12.5 mm graphite Raschig rings (cut from Morganite EY110 graphite tube), adjacent layers again being separated by 1 mm PVC mesh. In scale-up studies the column was packed with 20, 34 or 48 layers of rings (producing 21, 35 and 49 cells with the feeder electrodes) and there were 28 rings per layer (total wetted perimeter 181 cm). The current feeders were 5 mm thick graphite discs drilled with a large number of 3 mm diameter holes to ensure the minimum of hold up. All experiments were performed with batch recycling [6, 9].

In each experiment the initial concentration of CN^- was about 300 ppm. Batch depletion experiments were made with the short tower, first with sodium cyanide alone, then with sodium cyanide made approximately pH 13 with NaOH, next with NaCN and 0.135 mol dm^{-3} NaCl, and lastly with CN^- and 0.135 mol dm^{-3} NaCl made approximately pH 13. In all cases the inventory of solution was 1 dm^3 and the flow rate 0.6 dm^3 min^{-1}.

The scaling-up experiments were performed in the larger tower with initial concentrations of 300 ppm CN^- and 0.135 mol dm^{-3} NaCl conditioned to pH 10.4; the inventory was 2 dm^3. Different flow rates (0.5, 1.0, 1.5, 2.0 dm^3 min^{-1}) and different applied voltages (2 and 3 V/layer) were used, in towers of different lengths (21, 35 or 49 layers).

The cyanide concentration was estimated by Liebig's method [12], which was shown to be satisfactory above about pH 8 under the conditions of these experiments. Below about pH 8, titration with $AgNO_3$ indicated much lower values of CN^- than were actually present. For example, a 300 ppm CN^- solution made up at pH 12.6 was acidified to pH 3 with HCl, when Leibig's method indicated 35 ppm CN^-; on neutralization the estimate increased rapidly at pH 7 and a value of 280 ppm was obtained at pH 12.4, the difference from the original value being accounted for by dilution. During the experimental runs the pH was measured to check the validity of the analysis, but the pH was not controlled.

4. Results and discussion

4.1. *Chemical variables; small tower*

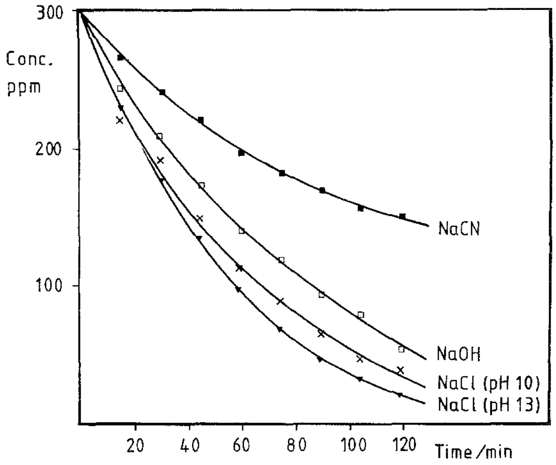

Fig. 1. Depletion of CN^- in small tower. 2.25 V/layer, 0.6 dm^{-3} min^{-1} flow rate.

Fig. 1 shows representative concentration–time plots for the four classes of experiment; it is clear that the direct oxidation is slowest. Since, in all the experiments reported here, Reaction 10 was the principal counter reaction, OH^- was continually produced and it is likely that OH^--dependent mechanisms (e.g. Reactions 7 and 8) made contributions to the removal of CN^- even in this case. Conditioning the NaCN solution to pH 13 with NaOH certainly increased the rate, but Fig. 1 shows that the indirect oxidation via electrogenerated hypochlorite (at pH about 9–10) was even faster; increasing the pH of the Cl^- solution still further increased the rate still more, probably due to the intervention of Reaction 13 which increases the effective active area for a fixed applied potential (see below). Since, in pollution abatement, it is undesirable to add reagents unless it is absolutely necessary in subsequent work the initial pH was fixed at 10.4. Fig. 2 shows how the contacting pattern in the trickle tower is favourable for the indirect oxidation; CN^- is convected inevitably into regions where HOCl is generated, while Reaction 8 is still an available path for any CN^- directly oxidized, OH^- being continuously generated by the counter reaction (Reaction 10) to replace that which is consumed. It was found that above pH 12 the pH tended to increase spontaneously, while below 12 it tended to decrease slowly due to the balance of the acid and alkaline shifts produced by the different reactions. Clearly parasitic reactions such as

$$2H_2O \rightarrow O_2 + 4H^+ + 4e \qquad 1.23\,V \quad (15)$$

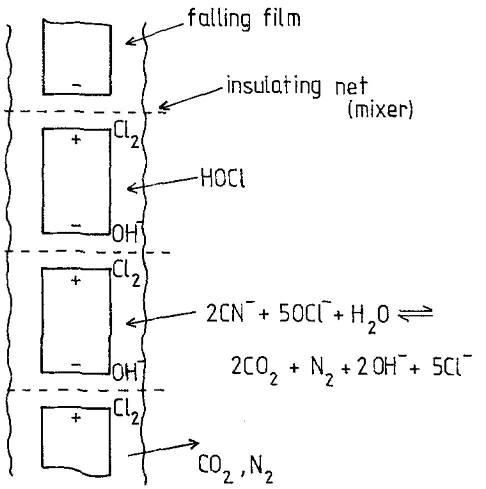

Fig. 2. Contacting pattern for hypochlorite generation and reaction with CN^-.

are also possible, although the overvoltage for oxygen evolution on graphite is high. Significantly a current efficiency of about 80% was obtained at pH 10 (2 V/layer), but this dropped to about 40% at pH 8 and pH 12.6.

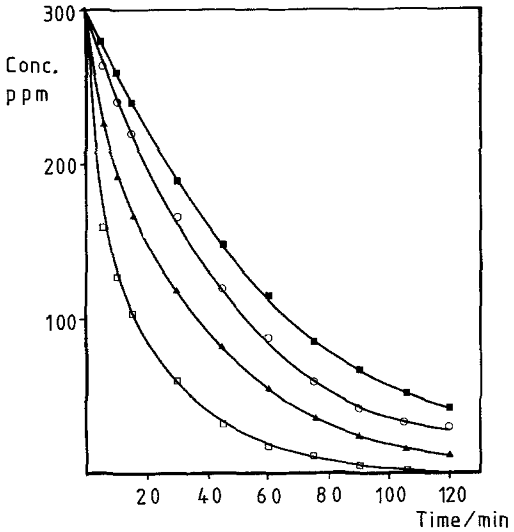

Fig. 3. Depletion of CN^- in large tower.

Symbol	*Number of layers*	*Voltage* (V/layer)	*Flow rate* ($dm^3\ min^{-1}$)
□	49	3	2
▲	49	3	0.5
○	21	2	1.0
■	21	2	0.5

4.2. *Engineering variables; large tower*

As might have been expected, the rate of removal of CN^- was a function of the number of layers of packing, the applied potential and the flow rate (Fig. 3). In all experiments there was a slow drift towards neutrality; plots of ln (c/c^0) versus time show a slight upward curvature towards low values of c, probably associated with this decreasing pH. Current efficiencies were slightly lower in the large than in the small tower.

In a trickle tower the cathodic and anodic overpotentials rise initially as hyperbolic sine functions [13], therefore the reaction at either extremity of an element rapidly comes under diffusion control and the relatively small zones of activation and mixed control can be ignored [14]. The trickle tower then behaves as a zoned reactor [6, 15] and the inlet concentration c_i is related to the outlet concentration c_o by

$$c_o = c_i \exp(-Kap\theta_L L/v_o). \qquad (16)$$

In batch recycling, if the reactor volume is insignificant compared with the inventory of solution, V, then the mass balance equation can be written

$$-\frac{dc}{dt}V = v_o c_i\,[1 - \exp(-Kap\theta_L L/v_o)] \qquad (17)$$

hence

$$K' = K\theta_L = \frac{v_o}{apL}\ln\left[1 + \frac{V}{v_o t}\ln\frac{c}{c^0}\right] \qquad (18)$$

where c^0 is the initial concentration. Table 1 shows the values of K' derived from the depletion experiments, assuming $a = 1.25$ cm and $L = 181$ cm. It can be seen that the values are still slightly dependent on the number of layers of elements, p, and flow rate, v_o; however, if estimates of θ_L are obtained using mass transfer coefficients derived from experiments on copper deposition in a similar tower [6], it can be seen (Table 1) that the apparent dependence on v_o is removed and Equation 17 describes the system reasonably well, i.e., Equation 16 can be used as a scaling law. The estimates of θ_L are of the same order as those observed in copper deposition [6] and the measurement of potential profiles [7] but the residual dependence of θ_L on p is unexplained unless it is due to the mean concentration being higher in shorter towers.

Table 1. Estimates of effective mass-transfer coefficient K' and fraction of area active θ for oxidation of CN^- in 0.135 M NaCl at pH 10; large tower

Voltage (V/layer)	*Number of layers*	*Flow rate* (dm^3 min^{-1})			
		0.5	*1.0*	*1.5*	*2.0*
		$10^4 K'$ (cm s^{-1})			
2	49	0.72	0.82	1.14	1.21
	35	0.85	0.99	1.12	1.29
	21	1.09	1.38	1.52	1.87
3	49	0.77	0.90	1.00	1.18
	35	1.00	1.15	1.36	1.57
	21	1.22	1.58	1.79	2.07
		Fraction of area active, θ			
2	49	0.11	0.11	0.13	0.12
	35	0.13	0.14	0.13	0.13
	21	0.17	0.19	0.18	0.19
3	49	0.12	0.12	0.12	0.12
	35	0.16	0.16	0.16	0.16
	21	0.19	0.22	0.21	0.20
		$10^4 K$ (cm s^{-1}) (from [6])			
		6.3	7.3	8.6	10.0

It is to be expected that θ_L will increase with applied voltage since it is given approximately by [6]

$$\theta_L = 1 - \frac{(\phi_s^R)^\circ}{\phi_s^T} \qquad (19)$$

where $(\phi_s^R)^\circ$ is the reversible potential of the electrochemical process at concentration c^0 of the electroactive species (Cl^- in most experiments) and ϕ_s^T is the potential across the ring, both with respect to the principal counter reaction. However, it can be seen from Table 1 that the effect is small. This is due to the fact that as the applied potential is increased to increase ϕ_s^T other reactions become possible (the current efficiency falls from 80% at 2 V/layer to about 35% at 3 V/layer) and the increased current produces a larger *iR* drop across the net separators; thus ϕ_s^T increases much less rapidly than the applied potential and the change in θ_L is relatively small. Naturally, any reaction which lowers $(\phi_s^R)^\circ$ increases θ_L and hence the effective rate constant K'. These effects probably explain why the rate increases with the addition of base; not only must Reaction 13 have a lower $(\phi_s^R)^\circ$ than Reaction 9 but the increased conductivity reduces *iR* drop so that θ_L is increased both by a lowering of $(\phi_s^R)^\circ$ and a raising of ϕ_s^T. A similar mechanism may explain the residual dependence of K' on p noted above. Because of the number of reactions which may take place in this system, no attempt was made to estimate $(\phi_s^R)^\circ$, as it was in a simpler system [6].

5. Conclusion

The destruction of CN^- by hypochlorite generated *in situ* in a bipolar trickle tower is essentially mass-transfer controlled and, to a reasonable approximation, Equation 16 can be used as a scaling law. The rate of reaction is accelerated by hydroxide ion, probably by its influence on the rate of hydrolysis of Cl_2 which leads to a reaction with lower reversible potential, hence to a larger fraction of the surface area being active. Above pH 12 the pH of a recirculating solution tends to drift upwards, while below pH 10 it tends to drift downwards, so that for large-scale processing a degree of pH adjustment is desirable.

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