

ELECTROCHEMICAL OXIDATION AS A TOOL FOR POLLUTION CONTROL : PART III STUDIES OF THE PACKED BED ELECTROLYSERS FOR THE DESTRUCTION OF CYANIDE

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ABSTRACT

Cyanides are potential pollutants even in traces and regulations limiting the cyanide concentration in industrial effluents down at 0.2 ppm and the permissible tolerance for inland surface waters at 0.01 ppm have been specified. Several investigations on the electrooxidation of cyanide in the effluent have been reported in literature. Use of three dimensional electrodes has been the recent development in this area of research.

In the present paper, a comparison of packed bed electrode cells of different configurations has been made for the anodic oxidation of cyanide. The initial concentration of electrolyte has been maintained at cyanide 200 ppm and NaCl 5 gpl. It has been observed that the packed bed cells of flow-bypass configuration function better than the flow through cells.

INTRODUCTION

Cyanide containing effluents are obvious ecological hazards and several regulations limiting cyanide in effluent have been in vogue. Major sources of cyanide pollution are from plating and metal finishing industries, iron and steel industries and photographic industries. Cyanide concentration in the effluent varies very widely between 50 and 1000 ppm even though the permissible tolerance limit is hardly about 0.01 ppm as per regulations [1]. As a consequence there has been intensive research, oriented towards destruction of cyanide in plant effluent by the most cost effective means. Electrochemical oxidation of cyanide both by direct and through hypochlorite has been reported in literature [2]. Application of trickle tower for the direct and indirect oxidation of cyanide [3] has been found to be fairly successful especially in presence of a base. It has also been found that the oxidation by *in situ* generated hypochlorite was faster than either direct oxidation or oxidation in presence of a base. The rate of oxidative destruction of cyanide has been found to be very much influenced by the presence of heavy metal ions such as copper, nickel, and cadmium [4]. Various other electrochemical reactors such as bipolar rotating electrode system, flowing system and packed bed electrode system have also been reported in the literature [5-7].

Flow through porous electrodes have recently been actively studied owing to their unusually large surface area and high mass transfer rate, which are the key parameters for designing high-space time yield electrochemical reactors. Several reports are available on the porous plate electrodes as well as the packed bed electrode for the study of electrochemical reactions in low concentration regime.

The packed bed electrode, because of its large surface area, is very well known to have high space time yield with respect to electrochemical reactions. It is also simple to set up and has low operating and maintenance cost. Because of these factors, these electrodes have received particular attention in recent years especially in applications involving very wide variation in concentration of the reactants [8]. Destruction of cyanide waste in the concentration range 0 to 1 M has been investigated using the packed bed electrochemical cell with flow-through configuration using steel

balls, at a temperature of 80°-95°C, and an average power consumption from 0.0025 to 0.05 kW per gm of cyanide destroyed, has been obtained. Chemical decomposition was also found to take place at the beginning of electrolysis due to reaction with the steel balls [7].

Earlier, investigations have been carried out with single packed bed electrolyser with flow through configuration for the anodic oxidation of cyanide [9]. The principle of electrochlorination has been followed for the electrolysis. It was observed that the cyanide concentration could be brought down to negligible value, and presence of chloride accelerated the rate of reaction.

With a view to find out the most efficient type of reactor for the removal of cyanide at low concentrations, < 200 ppm, different packed bed reactors, of both flow-through as well as flow-bypass configurations have been investigated and the results are reported in this paper.

EXPERIMENTAL

In fig. 1 the different cell configurations used in the study are shown schematically.

Cells A1, A2, and A3 belong to the category of flow-through configuration and B1, B2 and B3 are of flow-bypass configurations.

The cell systems consisted of packed bed working electrode which is composed of graphite particles of approximately 3 mm size and the particles are of irregular shape. In all the cells the characteristics of the packed bed electrode is maintained more or less constant. The volume of the packed bed is approximately 54 c.c. with 41% porosity. The cell volume is 140 cc. and that of the reservoir is 10 l.

Cell A1, consists of a single packed bed anode with a plane graphite cathode kept at the top. The interelectrode distance as measured from the top of the bed is 2.5 cm.

In Cell A2, two counter electrodes are provided on either side of the single packed bed anode and positioned at equal distance from either surface of the bed. The electrical contact for the

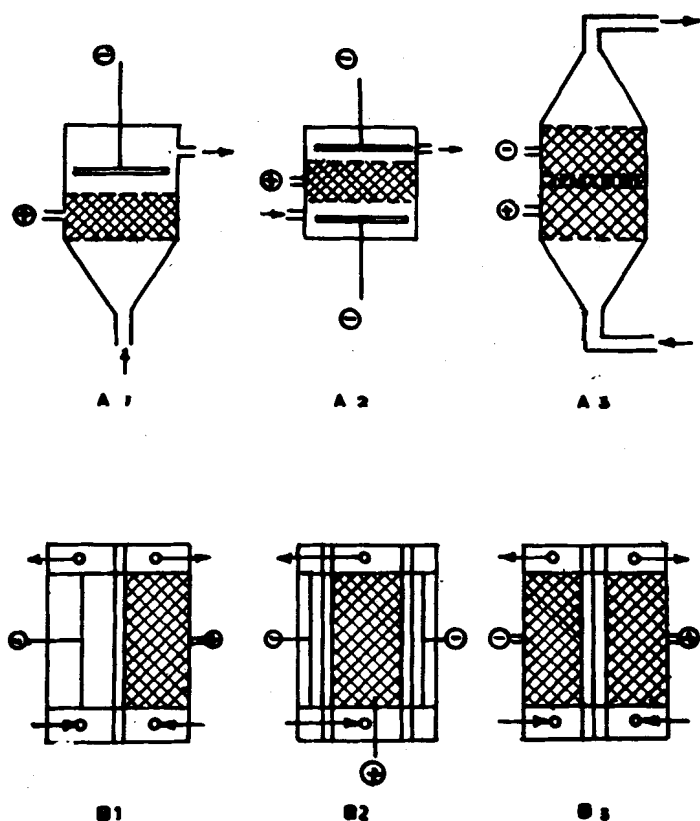


Fig. 2 : Schematic diagram of various cell configurations
 A. Reactors with flow-through configuration
 B. Reactors with flow-bypass configuration.

packed bed is provided through a graphite contact probe fixed in the middle of the cross section of the bed. In both these cells the packed bed is kept in form by means of perforated glass disc on both sides.

The counter electrode for the cell A3 is made up of another packed bed electrode similar to that of working electrode with a perforated glass disc separating the two electrodes. In all the three cells the bed height is 4.5 cm and the electrolyte is pumped from the bottom and the outflow is returned back to the reservoir.

As mentioned above, cells of group B are based on cross configuration wherein the electrolyte flow is perpendicular to the direction of current flow. The cells are fabricated out of PVC with perforated PVC separators to separate the anode and cathode chambers. Cell B1 consists of single packed bed working electrode with a planar counter graphite electrode. Cell B2 is composed of a central single packed bed anode with two planar graphite cathodes kept on either side of the working electrode. In cell B3 both the counter and working electrodes are packed bed electrode systems similar in construction and separated by PVC separator. In all the three cells, the electrolyte (anolyte and catholyte) is flown from the bottom and the out-flow is returned to the reservoir. Thickness of the bed in all the three cells is 1.2 cm and height of the bed is 9 cm.

The electrolyte was prepared by dissolving NaCN and NaCl and the initial composition of electrolyte was fixed at 200 ppm cyanide and 5 gpl NaCl. Based on the earlier investigations, the flow rate for the electrolyte was fixed at 60 l/hr and the electrolysis was carried out for 6 hrs at a constant applied voltage of 30V. The concentration of cyanide during electrolysis was estimated by drawing samples from the reservoir at 1 hr interval, using potentiometric titration method.

RESULTS AND DISCUSSION

The results are presented in Tables I and II and fig. 2. In table I average current obtained for each cell configuration at a constant applied voltage of 30 volts is given. It can be seen from the Table

Table I : Results obtained with packed bed electrolyser of different configurations in the anodic oxidation of cyanide.

Sl.No.	Flow-through configuration cells			Flow-bypass configuration cells		
	A1	A2	A3	B1	B2	B3
1. Average current amp (at 30 volts)	0.9	1.9	1.1	3.33	3.22	5.58
2. Concentration, ppm Initial	223	190	214	229	206	201
After 6 hours electrolysis	130	87	124	58	31	41
3. Current efficiency %	85	45	67	43	46	24
4. Conversion efficiency %	42	54	42	87	85	80
5. Mass transfer coefficient m cm/sec, 10 ⁻⁴	4.223	6.542	3.839	8.867	15.116	11.118
6. Spacetime yield ppm/cc/sec	0.986	1.528	0.904	2.071	3.531	2.507

Table II : Data on the performance of different cell configurations

Cell configuration	Cyanide concentration (ppm)		Time (hours) to bring down the CN ⁻ concentration to the level of (calculated)		
	Initial	After 6 hrs electrolysis	10 ppm	1 ppm	0.1 ppm
A1	223	130	31	54	77
A2	190	87	31	34	49
A3	214	124	33	58	83
B1	229	58	16	27	39
B2	205	31	9	16	23
B3	201	41	12	22	31

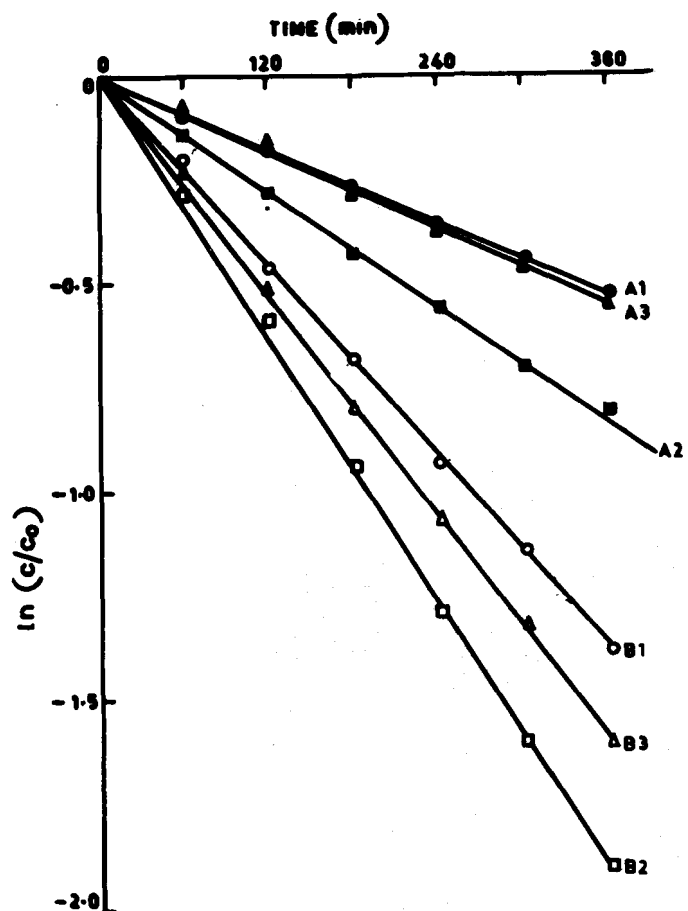


Fig. 2 : Logarithmic plot of C/C₀ with time

Note : A1 to A3 and B1 to B3 refer to the reactors used as given in Fig. 1

that the current obtained in flow by-pass cells, B1 and B2 is nearly 3 times that of flow-through cells, whereas the current obtained with B3 is nearly five times. Among the three cells of A series, the single packed bed cell with two counter electrodes, A2 seems to be better than the other two. In the case of Double Packed bed cell, A3, there is not much improvement in the current flow; the reason for this may be mainly that the entire packed bed is not fully utilised for the oxidation and most probably only the part of the bed facing directly the anode is effective as established by earlier workers [10]. Maximum current could be obtained with double packed bed cell of flow-bypass configuration namely B3.

In the same Table, are given the concentration of cyanide for 6 hours of electrolysis, overall current efficiency of the process conversion efficiency, mass transfer co-efficient *k* and space-time yield for the different reactors under study. It is evident from the Table that the concentration of cyanide was brought down considerably in the flow-bypass cells. The cells A1 and A3 have been found to behave more or less similarly, with a slight improvement in A3. The concentration of unreacted cyanide has been found to be minimum with B2 and has been in the order B2 < B3 < B1 < A2 < A3 < A1.

The current efficiency was calculated on the basis of cyanide oxidation and has been found to be the lowest for cell B3

whereas conversion efficiency, has been found to be fairly high for the same, namely, 80%. The conversion efficiency for cyanide destruction based on the concentration after 6 hours of electrolysis has been maximum with B2.

Treating the packed bed electrode unidimensionally, the mass balance in the direction of flow along the *y*-axis, the amount of cyanide reacted, *dM*, in the differential volume *A dy* is equal to

$$-dM = \frac{ai}{nF\Sigma} dy = \frac{-Q}{\Sigma A} dC \quad (1)$$

where *M* is the amount of cyanide, *C* is the concentration of cyanide at *y*, *Q* is the volumetric flow rate, *A* is the cross-section area across flow, Σ is the voidage *a* is the specific surface area of the bed and *i* is the current density at the electrode surface. The axial change in concentration is given by

$$\frac{dC}{dy} = -\frac{Aai}{nFQ} \quad (2)$$

In the packed bed the reaction comes under diffusion control because of low concentration of cyanide and flow of electrolyte. The effect of activation and mixed control can be ignored. Then

$$i = nFkC \quad (3)$$

where *k* is the mass transfer coefficient. Substituting equation (3) for *i* in equation (2),

$$\frac{dC}{C} = -\frac{k_a A}{Q} dy \quad (4)$$

which is integrated adopting the boundary condition *C* = *C* at *y* = 0 and *C* = *C'*, the outlet concentration i.e. concentration at the end of electrode at *y* = *L*, leads to the equation

$$C' = C \exp \left(\frac{-kaAL}{Q} \right) \quad (5)$$

In a batch recirculation, if the reactor volume is insignificant compared with the inventory solution volume *V*, the mass balance can be written as

$$-V \frac{dC}{dt} = QC - QC' \quad (6)$$

Substituting for *C'* from Eq (5)

$$-V \frac{dC}{dt} = QC \left\{ 1 - \exp \left(\frac{-kaAL}{Q} \right) \right\} \quad (7)$$

Hence,

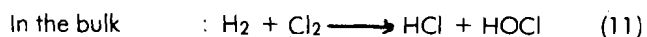
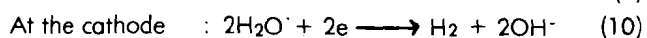
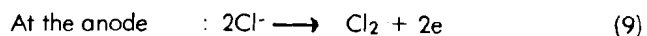
$$C = C_0 \exp \left\{ -\frac{t}{\tau} \left[1 - \exp \left(\frac{-kaAL}{Q} \right) \right] \right\} \quad (8)$$

where *C*₀ is the initial concentration, *V* is the volume of the reservoir and $\tau = V/Q$

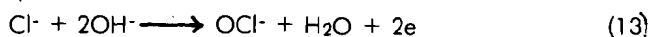
In fig. 2, the ln(*C/C*₀) vs *t* is presented for the different configurations. It is evident that the concentration decreases exponentially with time. Mass transfer coefficient was calculated, from the slope of the curves and are given in Table I. From the mass transfer coefficient, the space time yield for the various reactors, has also been computed and presented in the same Table. The value of *k* was found to be maximum for cell B2 and decreases in the order B2 > B3 > B1 > A2 > A1 > A3 and accordingly the space time yield calculated therefrom also shows the same trend. Based

on this coefficient, the probable time required for bringing down the cyanide concentration to 10 ppm, 1 ppm, and 0.1 ppm were computed and presented in Table II. It is clear from the Table that the cell with single packed bed working electrode with two counter electrodes following the flow-bypass configuration (B2) will require minimum time for complete removal of cyanide contaminant.

The reaction mechanism underlying the oxidation of cyanide has been investigated in presence of chloride and reported in literature [2]. Several reaction schemes have been proposed and it has been reported that electrooxidation of cyanide in presence of chloride ions occurs through hypochlorite. Under neutral conditions the formation of hypochlorite is possible [3] according to the following reactions :



During the electrolysis the pH of the electrolyte was found to increase indicating build up of alkali in the solution. It is also known that under alkaline conditions, the following reaction takes place :



In either event, the overall reaction with NaCN can be written as

$$2\text{NaCN} + 5\text{HOCl} \longrightarrow 2\text{CO}_2 + \text{N}_2 + \text{H}_2\text{O} + 3\text{HCl} + 2\text{NaCl} \quad (14)$$

The exact reaction mechanism is yet to be confirmed.

In conclusion, the packed bed cells with flow-bypass configuration have been found to function better than flow through cells under the conditions of study. Though the cell of the type B3 is capable of giving better current distribution and considerable high current for the given cell volume, it is observed that there is loss in current efficiency due to considerable current being used up for extraneous reactions such as chlorine evolution, rather than oxidation of cyanide. It may be possible to use this configuration also, with necessary alterations in conditions to minimise the extraneous reactions, which is yet to be studied.

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