Electrolytic Treatment of Cyanide Wastes VI. Effect of the Bed Height of a Fluidized Bed Electrode Cell on the Electrolytic Oxidation of Cyanide Ion

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Abstract

Electrolytic treatment of dilute cyanide wastes ($< 0.1 \text{ g} \cdot \text{dm}^{-3} \text{CN}^-$) was carried out in a fluidized bed electrode (FBE) cell having graphite particles, and the effects of the bed height, H_f , and the cell current, I_c , on the direct oxidation of CN^- were investigated. With increasing H_f the electrochemically active particle zone became thicker to bring higher current efficiency of CN^- decomposition. The increase in H_f reduced effectively both the time and the electrical energy required to attain the decomposition of 99%. The energy consumption increased almost proportionally to I_c .

1 INTRODUCTION

Previously, we examined factors for the electrolytic detoxication of dilute cyanide wastes ($\leq 0.1 \text{ g} \cdot \text{dm}^{-3}$)¹⁻⁴. By using an FBE anode with enlarged effective electrode area³, the waste treatment could be achieved in a short time and with reduced consumption of electrical energy. In an FBE cell, however, there remained a problem that the lower current efficiency was obtained at the larger cell current owing to the localization of the electrochemical reaction zone in the neighborhood of a collector electrode. As an attempt to overcome this problem, the anodic oxidation of chloride ion showing a high current efficiency even at a high current density^{5,6} was applied for the indirect oxidation of CN^- ⁴. However, this method has also a disadvantage that Cl^- , which causes the corrosion of steel, the evolution of Cl_2 , etc., remains in a treated solution at a high concentration.

In this study⁷), the effect of the bed height, H_f , on the rate of the direct oxidation treatment of CN^- in an FBE cell was investigated.

2 EXPERIMENTAL

2.1 Anodic oxidation of CN^-

The electrolytic decomposition of CN^- to CNO^- is shown by Eq. (1).

At $\text{pH} \leq 10$, formed cyanic acid ion CNO^- is decomposed by the reaction (2). Moreover, the oxygen evolution reaction (3) competes with the reaction (1) and lowers the current efficiency of CN^- decomposition. In this paper, this current efficiency is reflected on the following decomposition ratio of CN^- , X .

$$X = \{(C_0 - C)/C_0\} \times 100 \quad (\%) \quad (4),$$

where C_0 and C are the CN^- concentrations before and after the electrolysis, respectively.

2.2 FBE cell

The concentric cylindrical cell employed was described previously³). As seen in Fig. 1, a graphite rod (1 cm in diameter) collector and a stainless steel sheet (0.35 mm in

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Fig. 1 Concentric cylindrical cell with a fluidized bed anode

- 1. Electrolyte flow
 - 2. Fluidized bed
 - 3. Distributor
 - 4. Rectifier
 - 5. Diaphragm (anion exchange membrane)
 - 6. Acrylate resin tube
- H_f : Height of FBE

thickness) counter electrode were located at the center and on the outer cylinder, respectively. The height of these electrodes was varied from 10 to 100 cm.

The graphite particles (mean diameter of 1.3 mm, density of $1.7 \times 10^{-3} \text{ g-dm}^{-3}$) were used as electro-conductive particles. By controlling the amount of graphite particles, the height of a fluidized bed, H_f , was varied between 10 and 100 cm. The bed expansion was constant at 20 % at an electrolyte flow rate of $0.042 \text{ dm}^3 \cdot \text{s}^{-1}$ corresponding to a linear velocity of $2.2 \text{ cm} \cdot \text{s}^{-1}$ based on the empty cell³⁾.

2.3 Electrolyte

A 10 dm^3 of KCN aqueous solution containing $0.1 \text{ g-dm}^{-3} \text{ CN}^-$ adjusted at pH 11.4 by NaOH was flowed through the cell from a bottom at 313 K and circulated back to the reservoir.

2.4 Electrolysis

The electrolysis was carried out at a constant current ranging from 1 to 10 A. The total quantity of electricity was measured by a coulometer. The concentration of CN^- was monitored by an ion-selective elec-

trode⁴⁾. The adsorption of CN^- on graphite could be neglected as in the previous work, and as reported by Yoshizawa *et al.*⁸⁾.

3 RESULTS AND DISCUSSION

3.1 Decomposition ratio, X

Figures 2 and 3 show the increases in X with the quantity of electricity at two different cell currents, where a broken line corresponds to the theoretical value ($X/\% = 100$ at 7417 C). With increasing H_f , the obtained curve approaches gradually to the theoretical line as seen in these figures. Thus, the increase in H_f raises the current efficiency, because it spreads the effective electrode area and hence reduces a local current density. At $60 \leq H_f / \text{cm}$, the reaction (1) proceeds almost theoretically up to $X/\% = 60$ (Fig. 3) or 80 (Fig. 2), although the loss of current becomes remarkable for further decomposition because of lowered CN^- concentration.

Fig. 2 Decomposition of CN^- at the cell current of 2 A

- : Theoretical line
- Bed height; $\circ$: 10 cm, $\triangle$: 20 cm, $\square$: 30 cm, $\bullet$: 40 cm, $\blacktriangle$: 60 cm, $\blacksquare$: 80 cm, $\diamond$: 100 cm
- I: empty cell 10 cm, II: empty cell 100 cm

The lines I and II in these figures show the results in an empty cell where a collector electrode has the length of 10 and 100 cm, respectively. Though X increases with the length of a collector electrode in an empty cell, it is small compared with those in an FBE cell. This fact reveals that graphite particles act as anode to enlarge effective electrode area.

If we assume that the effective area is proportional to H_f , the average current density at $H_f = 100$ cm and $I_c = 10$ A is equal to that $H_f = 20$ cm and $I_c = 2$ A, and the same value of X will be expected in these two cases. As seen in Figs. 2 and 3, however, this is not the case which may be ascribed to the phenomenon that the more wide-spread radial distribution of a current density was observed at the smaller cell current, in other words, the electrochemical reaction zone is restricted the more closely to a collector electrode when the larger cell current is applied³). As a conclusion, the increase in H_f lowers the current density on a collector electrode and the active particles, and thereby makes the active particles zone thicker to bring a higher value of X .

Fig. 3 As Fig. 2 excepting the cell current of 10 A

Fig. 4 Relation between the cell voltage and the inverse of a bed height

Cell current; ●: 10 A, ▲: 5 A, ■: 2 A

3.2 Cell voltage, V_c

As shown in Fig. 4, the cell voltage, V_c , decreases linearly with the inverse of H_f . Thus, the following empirical relationship will hold.

$$V_c = K/H_f + \text{const.} \quad (5)$$

where the constant of K depends on the cell current as seen in this figure and presumably also on the electrical resistance of an electrolyte, the bed expansion, the material of particles and electrodes, etc. The increase in H_f has a technological merit to reduce V_c as described by Eq. (5).

3.3 Treatment time, t_{99}

The treatment time, t_{99} , defined as the electrolysis time required to decompose 99 % of the initial amount of CN^- (0.1 g-dm^{-3} , 10 dm^3), was shown in Fig. 5 as a function of H_f . As seen in this figure, t_{99} for each I_c is reduced by about 50 % by the increase in H_f from 10 to 60 cm. At $60 \leq H_f / \text{cm}$, t_{99} is shortened slightly with H_f . Anyway, it is pointed out that the increase in H_f up to 60 – 80 cm will be enough to minimize t_{99} effectively.

Fig. 5 Relation between the treatment time and a bed height
(keys as in Fig. 4)

3.4 Energy consumption, E_{99}

The energy consumption, E_{99} , defined as the supplied DC electrical energy to an FBE cell during the period of t_{99} , are shown in Fig. 6. As seen in this figure, E_{99} decreases with H_f rapidly at $H_f/\text{cm} \leq 60$ and slightly at $60 \leq H_f/\text{cm}$. Furthermore, Fig. 7 shows that the following relationship holds empirically.

$$E_{99}/H_f = 1.39 \times 10^3 I_c^{1.03} H_f^{-2.11} \quad (6)$$

Rearranging Eq. (6),

$$E_{99} = 1.39 \times 10^3 I_c^{1.03} H_f^{-1.11} \quad (7).$$

This equation shows that E_{99} is almost proportional to the cell current and to the inverse of a bed height. Eq. (7) is useful to predict the energy consumption in an FBE cell where the particles are dispersed uniformly with the bed expansion of 20%. This equation is useful also to predict H_f for any given E_{99} and I_c at a constant bed expansion of 20%.

Fig. 6 Relation between the energy consumption and a bed height
(keys as in Fig. 4)

Fig. 7 Linearized relation between the energy consumption and a bed height
(keys as in Fig. 4)

4 CONCLUSION

The operation factors for the direct oxidation of dilute cyanide wastes ($\leq 0.1 \text{ g-dm}^{-3} \text{ CN}^-$) in an FBE cell were investigated.

1. The increase in a bed height gave technological merits to raise the current efficiency and to reduce the cell voltage.
2. The required DC electrical energy to reduce CN^- down to the level of 1 mg-dm^{-3} was virtually proportional to the cell current and to the inverse of a bed height.

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