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Electrolytic oxidation of cuprocyanide electroplating waste waters under different pH conditions

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The main purpose of this work was to investigate the electrolytic oxidation of cuprocyanide solution with various total cyanide to copper molar ratios ranging from 2.8 to 20 and under different pH conditions. In strong alkaline solution (pH $\geqslant$ 12), cuprocyanide ions $Cu(CN)_n^{(n-1)-}$, where $n = 2$, 3 or 4, are directly electroxidized, and copper oxide precipitates on the anode. Cyanate ions, as well as nitrogen gas, were detected as the products and 0.30–0.43 g mol of total cyanide was destroyed per Faraday. For less alkaline solutions (pH < 12), cuprocyanide ions first dissociated to free cyanide ions and then electroxidized. At a pH of 10.5–11.7, cyanate ion and brown azulmin polymer were produced in the anolyte. In the neutral solution (pH = 7.0–8.6), carbonate and ammonium ions and azulmin were formed and 0.52–0.56 g mol of total cyanide was destroyed per Faraday. In weak acidic solution (pH = 5.2–6.8), oxalate and ammonium ions and white oxamide were produced and 1.01–1.18 g mol of total cyanide were destroyed per Faraday.

Nomenclature

C_{CN}	molar concentration of total cyanide ($kmol\,m^{-3}$)
C_{Cu}	molar concentration of total copper ($kmol\,m^{-3}$)
C_d	equivalent concentration of cyanide destroyed due to the formation of cupric oxide ($kg\,m^{-3}$)
C_f	concentration of cyanide destroyed by dissociation of complex ion to free cyanide ion and then electroxidized ($kg\,m^{-3}$)
C_i	initial concentration of total cyanide ($kg\,m^{-3}$)
C_t	change of total cyanide concentration during electrolysis ($kg\,m^{-3}$)
F	Faraday constant ($96\,487\,C\,mol^{-1}$)
K_1, K_2, K_3	formation constant of dicyanocuprate, tricyanocuprate and tetracyanocuprate ions
R	molar ratio of total cyanide concentration to total copper concentration (i.e. C_{CN}/C_{Cu})
W	weight of precipitates on electrodes or in anolyte (kg)
θ	angle of incidence

1. Introduction

The effluent waste waters from electroplating and metallurgical processes frequently contain different forms of cyanides. Cyanide waste is generally treated with chlorine, sodium hypochlorite, etc. However, there are several disadvantages with this type of treatment: (i) it is expensive; (ii) it is not so effective for cyanide complex wastes; (iii) it produces a large quantity of sludge.

Electroplating waste water containing metal cyanide can be decomposed by electrochemical oxidation. In 1913, Kern [1] and Clevenger [2] first reported the electrolytic oxidation of KCN solution using different electrodes. In early work, Oyler [3] and Sperry and Cladwell [4] reported the disposal of cyanide-complex waste liquid by electrolytic oxidation. There are numerous subsequent papers describing cyanide decomposition based on *in situ* liberation of hypochlorite by electrolysis of a cyanide waste in the presence of dissolved chloride [5–13]. This technique is suitable for destroying cyanide in dilute waste water (less than 500 p.p.m.). Other papers report direct electrolytic oxidation for destroying strong cyanide solution (greater than 1000 p.p.m.) [13–30]. Plate-type electrodes have usually been applied in electrochemical cyanide destruction studies. In recent years other electrodes have been investigated, such as fluidized-bed [20], packed-bed [22–24] and barrel electrodes [21].

It has been accepted that free cyanide ions are electrochemically oxidized at the anode by first forming free cyanide radicals [23, 25–29]

$$CN^- \longrightarrow CN^{\cdot} + e \qquad (1)$$

Free cyanide radicals then proceed to decompose. Some investigators have reported that cyanogen is formed in acid solution [25] and cyanate ion [1–4, 13–30], carbonate ion [7, 13–16, 27–30], azulmin [31], etc. have been found as products in alkaline solution.

Two views on the electroxidation of the cuprocyanide complex ion have been reported in the literature. One is that the complex ion goes through an indirect oxidation step, i.e. the complex ions first dissociate to free cyanide ions and are then oxidized. Dart *et al.* [27] proposed that free cyanide ions are produced by dissociation of the complex according to the reaction

$$Cu(CN)_4^{3-} = Cu + 4CN^- \qquad (2)$$

It was assumed that Equation 2 proceeds sufficiently fast and is not the rate-limiting step. Sperry and Cladwell [4] and Easton [14] reported that the source of cyanide ion is the dissociation of the complex due to copper deposition on the cathode:

$$Cu(CN)_3^{2-} + e = Cu + 3CN^- \qquad (3)$$

Other workers have reported that complex ions undergo direct electrolytic reaction [6, 7, 24, 30]:

$$Cu(CN)_3^{2-} + 6OH^- = Cu^+ + 3CNO^- + 3H_2O + 6e \qquad (4)$$

Tan *et al.* [24] electrolysed copper cyanide electrolyte consisting of $CuSO_4$ and KCN and proposed the reaction

$$Cu^+ + 2OH^- = CuO + H_2O + 2e \qquad (5)$$

An overall oxidation mechanism in different compositions is not clear in the existing literature. The main purpose of this work was to establish the reaction mechanism by analysing the electrolytic oxidation products in the cuprocyanide solutions with molar ratios, R, ranging from 2.8 to 20 and under different pH values (pH = 5.2–14).

2. Experimental details

Sodium cyanide and cuprous cyanide of reagent grade were dissolved in 60 cm^3 of deionized water to prepared solutions containing 5 kg m^{-3} of total cyanide with different C_{CN}/C_{Cu} molar ratios. The pH was further adjusted by addition of sodium hydroxide to form strong alkaline cuprocyanide solutions of pH 12, 12.5, 13.4, etc. Ammonium chloride was used to control the pH between 7.48 and 8.50. For neutral and weak acidic solution, $K_2HPO_4 + KH_2PO_4$ and HOAc + NaOAc were used to adjust the pH.

A Pyrex electrolytic cell consisting of two platinum electrodes (3.4 × 4.0 cm^2) with a separation distance of 4.4 cm was set up. The anolyte and catholyte compartments were separated by a sintered glass partition and contained 50 cm^3 and 10 cm^3 of electrolyte, respectively. A saturated calomel reference electrode (SCE) was positioned 0.2 cm from the anode plate. The anolyte was thoroughly de-oxygenated by purging with helium gas. Direct current was supplied by a potentiostat (Nichia

NP-1000E, Japan) at 35° C. Before electrolysis the platinum electrodes were pickled in 10% HNO_3 for 3 min, then washed with deionized water. The cell was covered to prevent the evaporization of electroyte during the electrolysis.

After electrolysis, for the strong alkaline solutions (pH $\geqslant$ 12), the precipitate on the anode was analysed by X-ray diffractometry (Shimadzu XD-5) and X-ray photoelectron spectroscopy (PHI Model 590 ESCA/SAM), respectively. The gas generated, due to anodic oxidation, was analysed by gas chromatography (Shimadzu-6A) with a molecular sieve 5A and triacetin columns. In the neutral, weak alkaline and weak acidic solutions, the precipitate in the anolyte compartment were decanted, centrifuged and vacuum dried, then analysed by means of an infrared spectrophotometer (Perkin-Elmer model 983), and an elemental analyser (Perkin–Elmer 240C), respectively. Analysis of CNO^- was executed by Raman spectroscopy (Spectra Physics Model 1700) with titrated with 0.1 N hydroxylamine hydrochloride and 2% ferrous chloride solution. Nessler's reagent (HgI_2 + KI), potassium permanganate solution and barium chloride were employed in the analysis of NH_4^+, $C_2O_4^{2-}$ and CO_3^{2-}, respectively.

For the determination of total cyanide, the sample solution was stored in a flask and treated with concentrated nitric acid. The released hydrocyanic acid gas was absorbed in a 0.1 N sodium hydroxide solution. The dissolved cyanide was titrated with a 0.01 M $AgNO_3$ solution with potassium iodide as indicator for the determination of free cyanide concentration.

3. Results and discussion

Cyanocuprate ions, $Cu(CN)_n^{(n-1)-}$ where n = 2, 3 or 4, in the aqueous solution undergo successive equilibrium steps as follows [32–34]:

$$Cu^+ + 2CN^- \overset{K_1}{\rightleftharpoons} Cu(CN)_2^- \tag{6}$$

$$Cu(CN)_2^- + CN^- \overset{K_2}{\rightleftharpoons} Cu(CN)_3^{2-} \tag{7}$$

$$Cu(CN)_3^{2-} + CN^- \overset{K_3}{\rightleftharpoons} Cu(CN)_4^{3-} \tag{8}$$

Here, $K_1 = 8.11 \times 10^{23}$, $K_2 = 1.99 \times 10^5$ and $K_3 = 31.8$ are the formation constants of dicyanocuprate, tricyanocuprate and tetracyanocuprate ion, respectively [32–34]. Since K_1 is very large, the Cu^+ concentration is much lower than in other cyanocuprate species. From the mass balance of Cu and CN species, we get

$$\frac{K_2K_3}{C_{Cu}}[CN^-]^3 + \left\{(4 - R)K_2K_3 + \frac{K_2}{C_{Cu}}\right\}[CN^-]^2 + \left\{(3 - R)K_2 + \frac{1}{C_{Cu}}\right)\right\}[CN^-] + 2 - R = 0 \tag{9}$$

where $R = C_{CN}/C_{Cu}$, C_{Cu} and C_{CN} are the total molar concentrations of copper and cyanide in the cuprocyanide solution. If the values of K_2, K_3, R and C_{Cu} are given, the concentration of free cyanide, $[CN^-]$, can be determined from Equation 9. By knowing the free cyanide concentration and the formation constants the concentration of different cyanocuprate ions can be calculated. In the solution, the predominant cuprocyanide ions are dependent on the value of R. For different ranges of R, the predominant cyanide ions are listed as follows:

$$Cu(CN)_2^-,\ Cu(CN)_3^{2-} \quad \text{for } 2 < R < 3 \tag{10a}$$

$$Cu(CN)_3^{2-},\ Cu(CN)_4^{3-} \quad \text{for } 3 < R < 4 \tag{10b}$$

$$Cu(CN)_4^{3-} \text{ and } CN^- \quad \text{for } R > 4 \tag{10c}$$

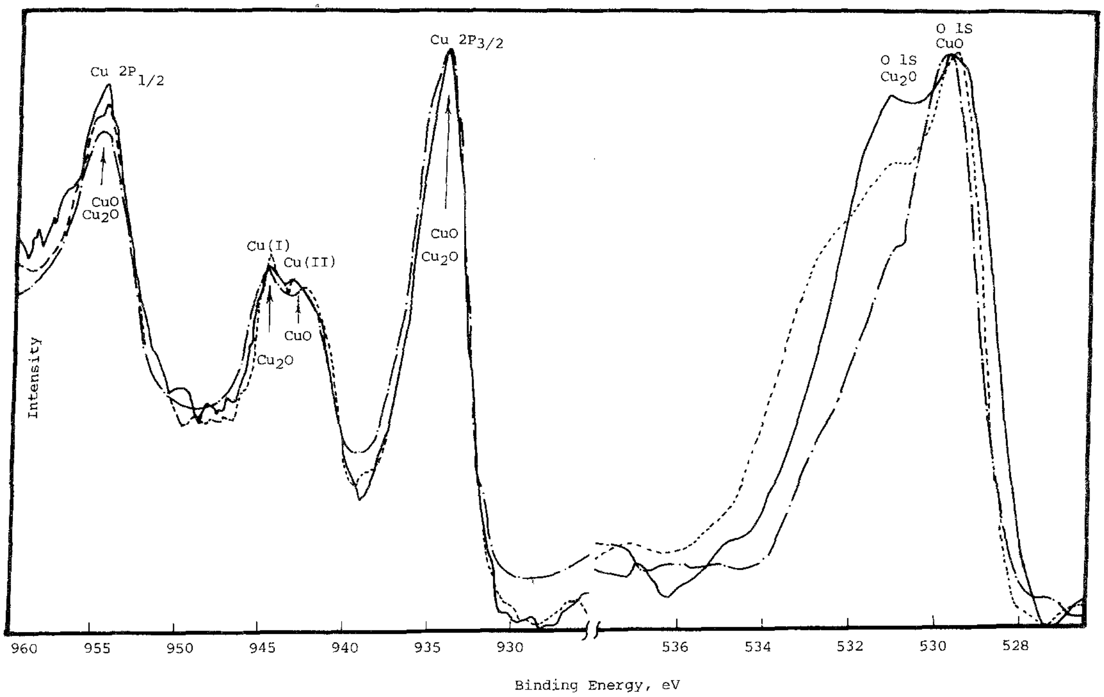


Fig. 1. X-ray photoelectron spectra of the precipitate deposited on the platinum anode in strong alkaline cuprocyanide solutions. ——, pH = 13.6, *R* = 2.8; – – –, pH = 12.0, *R* = 3.5; –·–, pH = 12.5, *R* = 4.2. Potential = 0.71 V versus SCE.

3.1. *In strong alkaline solution (pH $\geqslant$ 12)*

The electrolytic oxidation of strong alkaline cuprocyanide solution ($C_i = 5\,\mathrm{kg\,m^{-3}}$, pH $\geqslant$ 12) with R ranging from 2.8 to 20, was carried out under constant potential electrolysis at 0.71 V versus SCE. A reddish black deposit on the platinum anode was observed during the electrolysis. The X-ray photoelectron spectra of the precipitate under various values of R and pH are given in Fig. 1. The peaks of the X-ray photoelectron spectra (Fig. 1) at 944.6, 943.0, 531.2 and 529.9 eV correspond to the binding energy of $\mathrm{Cu_{Cu_2O}}$, $\mathrm{Cu_{CuO}}$, $\mathrm{O_{Cu_2O}}$ and O_{CuO}, respectively. Both XPS spectra and X-ray diffraction patterns, as shown in Fig. 2a and b, indicate that the reddish black precipitate on the anode are composed of red cuprous oxide and cupric oxide. The cyanate ion ($\mathrm{CNO^-}$) is generated in the strong alkaline cuprocyanide solution after electrolysis as shown by the Raman spectra of Fig. 13b. The peaks at 1200, 1300 and 2150 $\mathrm{cm^{-1}}$ correspond to the symmetric and asymmetric stretch of the cyanate ion ($\mathrm{CNO^-}$), respectively [25]. The peaks at 1625 and 2075 $\mathrm{cm^{-1}}$ (Fig. 3a, b) correspond to the Raman absorption of H_2O and $\mathrm{C \equiv N}$, respectively [25].

In view of these experimental results, it is proposed that the anodic reaction mechanism during the electrolysis is

$$\mathrm{Cu(CN)}_n^{(n-1)-} + 2n\mathrm{OH^-} = \mathrm{Cu^+} + n\mathrm{CNO^-} + n\mathrm{H_2O} + 2ne \tag{11}$$

where $n = 2$, 3 or 4.

The cuprous ion on the anode surface is unstable and instantly reacts with hydroxyl ion to form cuprous oxide

$$2\mathrm{Cu^+} + 2\mathrm{OH^-} = \mathrm{Cu_2O} + \mathrm{H_2O} \tag{12}$$

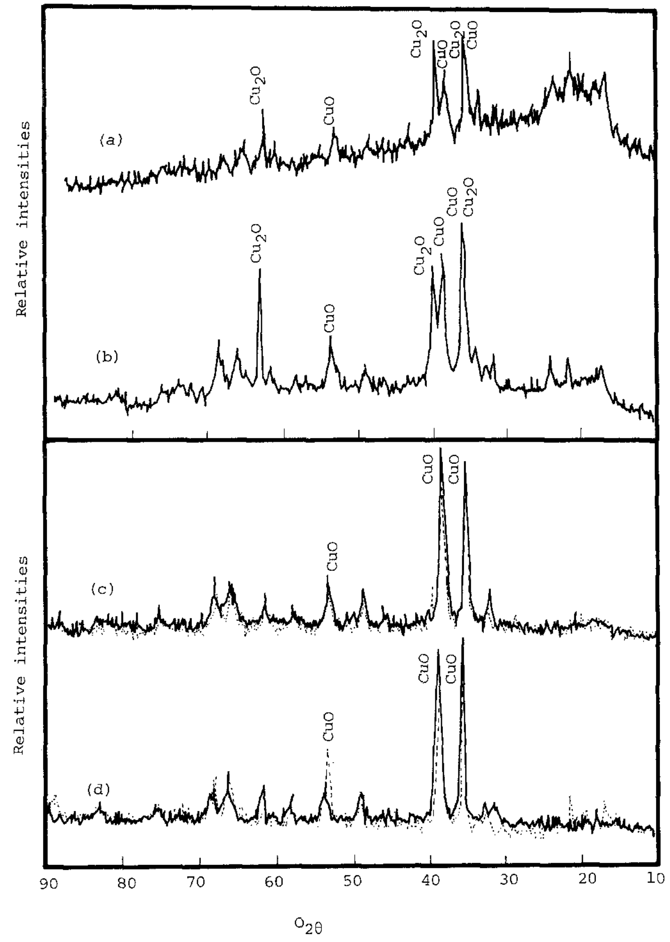


Fig. 2. X-ray diffraction patterns of precipitates on the platinum anode for electrolytic oxidation of strong alkaline cuprocyanide solutions. (a) pH = 13.6, R = 2.8. (b) pH = 12.0, R = 3.5. (c) ——, pH = 13.8, R = 10; - - -, pH = 13.4, R = 3.5. (d) ——, pH = 12.5, R = 4; - - -, pH = 13.4, R = 4). Potential: (a, b) 0.71 V versus SCE; (c, d) 1.2 V versus SCE.

Part of the cuprous oxide is again electrochemically oxidized to cupric oxide

$$Cu_2O + 2OH^- = 2CuO + H_2O + 2e \qquad (13)$$

These equations explain the phenomena of red Cu_2O and black CuO formation on the anode. When electrolysis was controlled at high potential (1.2 V versus SCE), only the black precipitate appeared on the platinum anode. Using X-ray diffraction the precipitate was verified as being cupric oxide (Fig. 2c, d). This is possibly due to the cuprous ion reacting directly with hydroxyl ion to form cupric oxide [24] instead of cuprous oxide as the intermediates.

For strong alkaline cuprocyanide solution with various values of R, the concentration change of total cyanide (C_t), and the weight of copper in cathodic and anodic precipitates, are summarized in Table 1. The weight of copper deposit on the cathode (W_{Cu}) is 24–45% of the anodic cupric oxide precipitate (W_{CuO}). The total recovery of copper from the two electrodes is approximately 59–90% of the total copper weight in the cuprocyanide solution before electrolysis. According to reactions 11–13 and 5, 1 g mol cupric oxide produced equals n g mol CN being oxidized. This n real value ranges from 2 to 4 and depends on R, as in Equation 10; for example, for R = 10 and 20 the n value is 4. From Table 1 it is found that the quantity of total cyanide destroyed (C_t) after electrolysis is more than the cyanide destroyed (C_d) due to the formation of cupric oxide. Undoubtedly, the surplus comes from the complex cyanide ion being first dissociated into free cyanide ion and then oxidized. Cuprocyanide complex ions in the aqueous solution not only obey the ionic equilibria

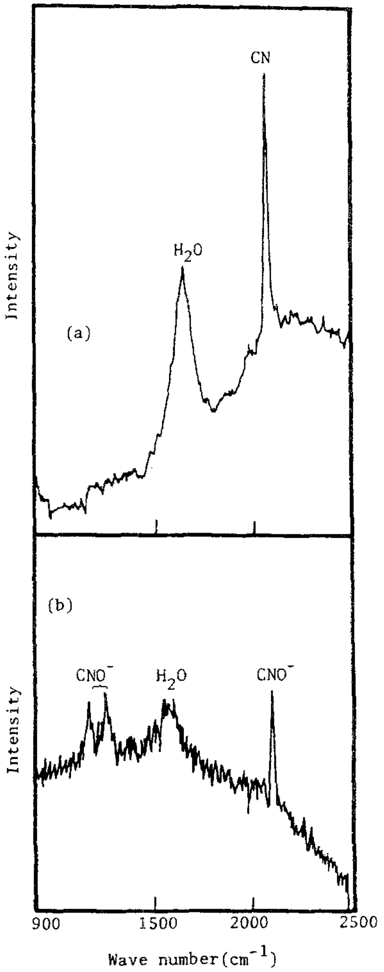


Fig. 3. Raman spectra of the strong alkaline cuprocyanide solution where $R = 4.0$ and pH = 12, (a) before electrolysis, (b) after electrolysis.

according to reactions 6 to 8 but also accept electrons from the cathode and then release free cyanide as follows:

$$\mathrm{Cu(CN)}_n^{(n-1)-} + e = \mathrm{Cu} + n\mathrm{CN}^- \tag{14}$$

where $n = 2, 3$ or 4.

Free cyanide ions in strong alkaline solution proceed, according to reaction 15, to produce cyanate ion [1–4, 13–30]:

$$\mathrm{CN}^- + 2\mathrm{OH}^- = \mathrm{CNO}^- + \mathrm{H_2O} + 2e \tag{15}$$

Table 1. Electrolytic oxidation of strong alkaline cuprocyanide solution at various R *when* $C_i = 5\ kg\,m^{-3}$*) and potential = 1.2 V versus SCE*

R	*pH*	*Quantity of electricity (F)*	C_t *(kg m^{-3})*	*Cathode* W_{Cu} *($\times 10^{-5}$ kg)*	*Anode* W_{CuO} *($\times 10^{-5}$ kg)*	C_d *(kg m^{-3})*	C_f *(kg m^{-3})*
2.8	13.2	0.0327	4.18	5.41	22.6	3.45	0.73
3.5	13.4	0.0261	3.63	4.94	16.5	3.15	0.48
4.0	12.5	0.0252	4.72	4.32	9.57	2.08	2.64
4.0	13.4	0.0238	3.54	3.87	13.3	2.89	0.65
10	13.8	0.0347	4.91	2.09	5.64	1.23	3.68
20	14.0	0.0236	3.89	0.96	2.85	0.62	3.27

For the same reason, free cyanide ions from the dissociation of cuprocyanide ion also follow reaction 15. Reactions 11 and 15 require one Faraday of electricity to destroy 0.5 g mol of total cyanide. Results in Table 1 show that one Faraday actually destroys 0.30–0.43 g mol of total cyanide. The difference is due to the fact that the current is partially consumed for the continuous oxidation of cyanate ion [7, 14–16, 22, 30] and the formation of cupric oxide. Therefore, in the strong alkaline cuprocyanide aqueous solution, it is reasonable to assume simultaneous occurrence of reactions 11–13, 5 and 15.

The generated gas was determined by gas chromatography with a thermal conductivity cell detector, using molecular sieve 5A and a porapak packing column. The flow rate of hydrogen gas as carrier gas was 10 $\mathrm{cm^3\,min^{-1}}$; injection, column and detector temperatures were controlled at 160, 40 and 160° C respectively. Two peaks at retention times of 0.49 and 0.83 min and volume percents of 7.2 to 92.8 were detected; these were confirmed as oxygen and nitrogen. The evolution of nitrogen gas implies that the cyanate produced in the solution was further oxidized to nitrogen. The reaction may be as follows

$$2\mathrm{CNO^-} + 4\mathrm{OH^-} = 2\mathrm{CO_2} + \mathrm{N_2} + 2\mathrm{H_2O} + 6e \tag{16}$$

Reaction 16 was also previously mentioned in other works [7, 14–16, 22, 30] without actual identification of the gaseous product. The oxygen evolution was caused by the discharge of hydroxyl ion as a side reaction,

$$4\mathrm{OH^-} = \mathrm{O_2} + 2\mathrm{H_2O} + 4e \tag{17}$$

Some investigators reported the existence of cyanogen (C_2N_2) in weak acidic cyanide solution. For strong alkaline solution (pH $\geqslant$ 12), cyanogen gas was not detected by gas chromatography using the triacetin packing column.

3.2. *In neutral or weak alkaline solution (pH = 7.0–11.7)*

The electrolysis of neutral or weak alkaline cuprocyanide solution was carried out under constant potential at 1.2 V versus SCE. It was found that brown precipitates were formed in the anolyte compartment. These were tested by infrared spectroscopy (see Fig. 4a) and elemental analysis. The weight proportions of C : H : N : O were 33.7 : 3.3 : 52.3 : 10.7. This result is in agreement with Fitzgerald's [31] report that the brown precipitate is azulmin. Hittorf [36] first proposed that, in the electrolysis of the alkaline cyanide solution, the brown anode deposit was due to the free cyanide radical being polymerized to form paracyanogen $(\mathrm{CN})_n$:

$$n\mathrm{CN}^{\cdot} = (\mathrm{CN})_n \tag{18}$$

Fitzgerald [31] reported that the precipitates were produced on platinum or carbon anodes but not on the lead anode. This study confirmed that the precipitates were azulmin formed by the polymerization of aqueous hydrocyanic acid in the presence of alkali. One coulomb of electricity produces 1.0×10^{-7} to 6.05×10^{-7} kg azulmin, as given in Table 2. The W/Q value is minimum when the pH is 11.7. The filtrate of the cuprocyanide solution (pH = 10.5–11.7) was titrated with 0.1 N hydroxylamine hydrochloride, and 2% ferrous chloride $\mathrm{CNO^-}$ was detected in the product. A portion of filtrate of the cuprocyanide solution (pH = 7.0–8.6) was titrated with barium chloride; $\mathrm{CO_3^{2-}}$ was detected in the solution. The remainder of the filtrate was titrated with Nessler's reagent and $\mathrm{NH_4^+}$ was detected in the product. Therefore it can be concluded that in the neutral or weak alkaline solution the cuprocyanide complex ion does not go through direct oxidation reactions 11 to 13. The complex first dissociates to free cyanide, according to reactions 14 and 6–8, and then cyanide ions are oxidized. The reaction mechanism may be as follows:

$$2\mathrm{CN}^{\cdot} = \mathrm{C_2N_2} \tag{19}$$

$$\mathrm{C_2N_2} + 2\mathrm{OH^-} = \mathrm{CNO^-} + \mathrm{CN^-} + \mathrm{H_2O} \tag{20}$$

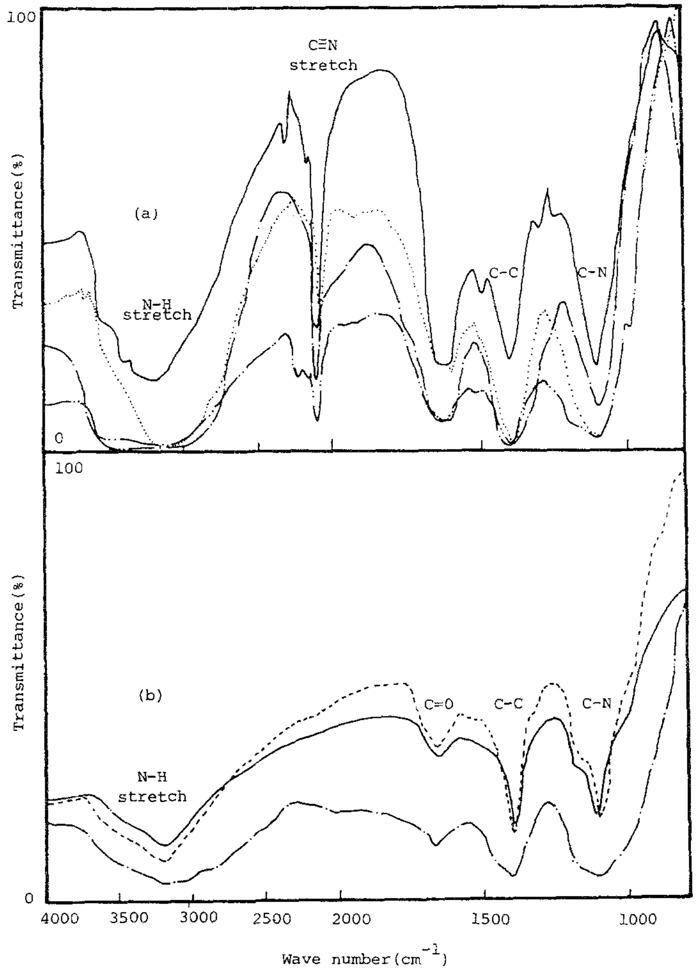


Fig. 4. Infrared spectra (KBr pellet method) of the precipitates formed in the anolyte compartment for electrolytic oxidation of cuprocyanide solutions. Potential = 1.2 V versus SCE. (a) ——, pH = 8.05, R = 3.5; –·–, pH = 7.48, R = 3.5; –··–, pH = 10.7, R = 3.5; ····, pH = 8.5, R = 10.0. (b) ——, pH = 6.8, R = 3.5; - - -, pH = 6.0, R = 2.8; –·–, pH = 5.2, R = 20.0.

Table 2. Brown precipitates formed in the anolyte compartment in the electrolytic oxidation of weak alkaline cuprocyanide solution at various R and pH

R	*pH*	*Quantity of electricity* (× 10^2 C)	C_t *(kg m^{-3})*	*Weight of precipitates* (× 10^{-4} kg)	*W/Q*[a] (× 10^{-7} kg C^{-1})
2.8	10.5	1.90	0.469	0.691	3.64
3.5	10.7	5.43	1.293	2.47	4.55
3.5	8.05	2.58	0.648	1.01	3.91
3.5	7.48	8.82	2.22	2.64	2.99
4.0	10.7	4.10	0.995	1.92	4.68
4.0	11.7	4.04	0.942	0.406	1.00
10	8.50	4.05	1.02	2.20	5.43
10	10.9	9.30	2.21	5.56	5.97
20	11.1	8.49	1.98	5.14	6.05

[a] The ratio of weight of precipitates (W) to quantity of electricity (Q).

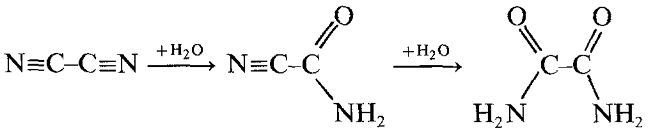
However, in the neutral solution (pH = 7.0–8.6) the cyanate ion may continuously undergo hydrolysis to produce ammonium and carbonate ion [37],

$$CNO^- + 2H_2O = NH_4^+ + CO_3^{2-} \tag{21}$$

The ammonium ion may react with more cyanates to form urea [3, 23, 27]. However, it is known that urea is hydrolysed in the presence of acids or bases to form carbonate and ammonium ions [38]. Reactions 1 and 19–21 imply that one Faraday of electricity destroys 0.5 g mol of total cyanide. The experimental results in Table 2 show that 0.52–0.56 g mol of total cyanide was destroyed per Faraday. This value is slightly higher than the theoretical prediction.

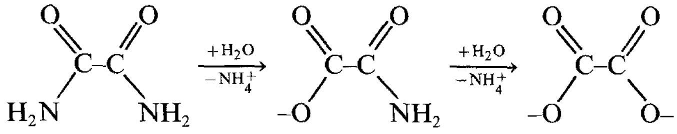
3.3. *In weak acidic solution (pH = 5.2–6.8)*

When the electrolysis was carried out in weak acidic cuprocyanide solutions, white precipitates were formed in the anolyte compartment. The weight of precipitates per Faraday decreased with decreasing pH, as given in Table 3. The precipitates were tested by infrared spectroscopy (Fig. 4b) This shows that the absorption peaks at 3100–3500, 1670, 1300 and 1100 cm^{-1} are consistent with the standard infrared spectroscopy peak spectra of oxamide $(CONH_2)_2$. The filtrate from the electrolysis was titrated with acidic 0.1 N potassium permaganate solution and Nessler's reagent, respectively. It was confirmed that oxalate and ammonium ions were contained in the product. The formation of white oxamide precipitates is possibly because the C_2N_2 formed by the coupling of CN radicals of reaction 19 is subsequently hydrolysed



(22)

Part of the oxamide, $(CONH_2)_2$, may be continuously hydrolysed in the presence of acids;



(23)

The combination of reactions 22 and 23 leads to

$$C_2N_2 + 4H_2O = C_2O_4^{2-} + 2NH_4^+ \tag{24}$$

Reaction 24 is consistent with reports of Dart *et al.* [27] and Arikado *et al.* [28] that the electrolytic oxidation of the simple cyanide ion forms oxalate and ammonium ion at low OH$^-$ concentration. Therefore, in the electrolytic oxidation of weak acidic cuprocyanide solution of pH from 5.2 to 6.8, the cuprocyanide complex ions $Cu(CN)_n^{(n-1)-}$, where $n = 2$, 3 or 4 first dissociated to free cyanide ion and then electroxidized. Reactions 1, 19, 22 and 24 represent the consumption of one Faraday of electricity for the destruction of 1 g mol of total cyanide. The experiment shows that 1.01 to

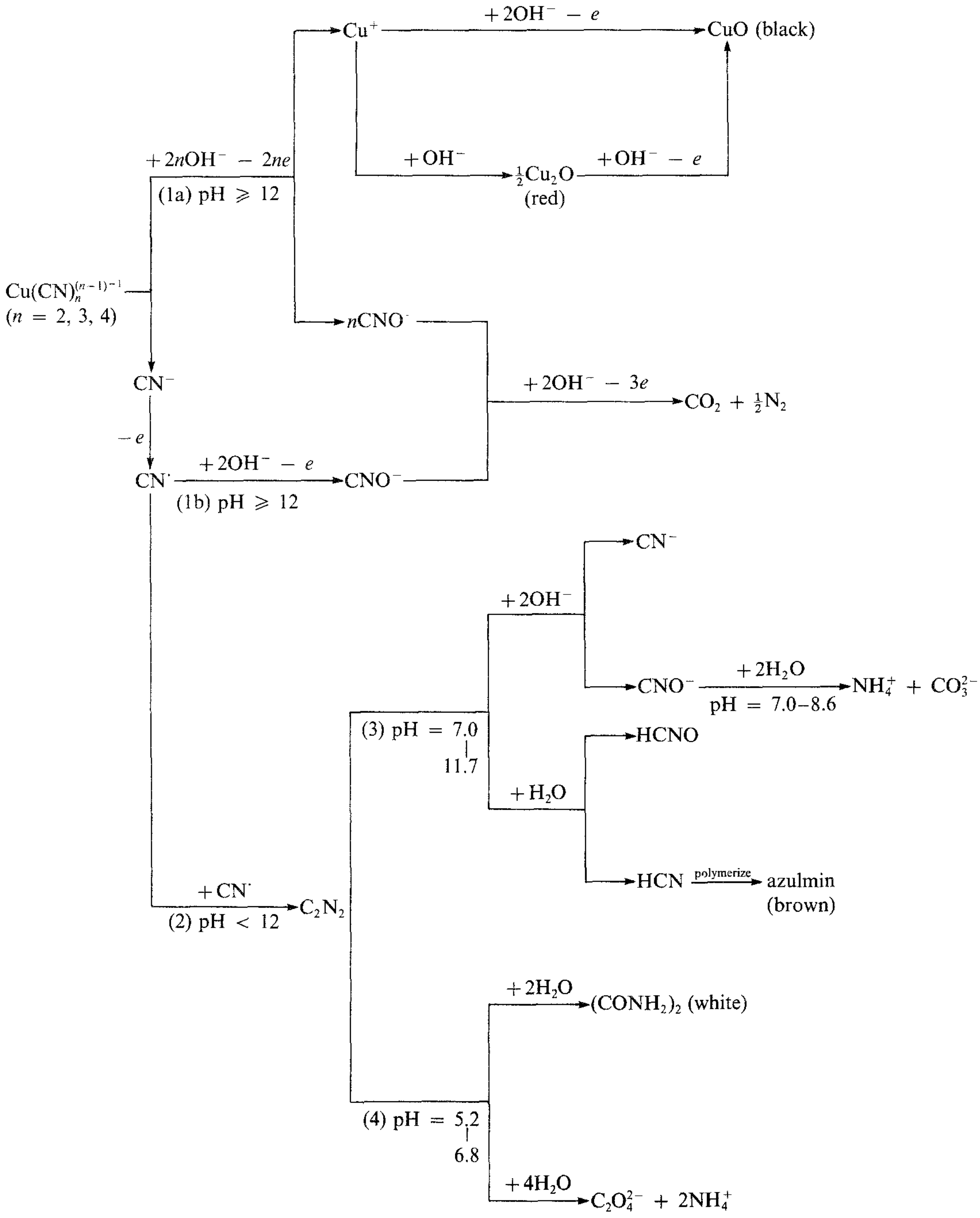
Table 3. White precipitates formed in the anolyte compartment in the eletrolytic oxidation of weak acidic cuprocyanide solution at different R

R	*pH*	*Quantity of electricity (C)*	*Weight of precipitates* ($\times 10^{-5}$ *kg)*
2.8	6.0	87.8	1.08
3.5	6.8	196.1	7.13
20	5.2	186.9	0.62

1.18 g mol cyanide is destroyed per Faraday. It is therefore proposed that reaction mechanisms 22 and 24 occur simultaneously.

4. Conclusion

The electrochemical oxidation of cuprocyanide proceeds via different mechanisms in different solutions. The reaction mechanisms can be summarized as follows:



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