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The electrochemical oxidation of alkaline copper cyanide solutions

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Abstract

A systematic investigation of the electrochemical oxidation of copper cyanide was carried out. At low pH, cyanide destruction is believed to be catalyzed by the heterogeneous reaction involving adsorbed $[\text{Cu}(\text{CN})_3]^{2-}$ and possibly $[\text{Cu}(\text{CN})_4]^{3-}$. At high pH, rapid oxidation of cyanide was observed around 0.75 V versus Hg/HgO with the formation of a black copper oxide film. This enhanced electrocatalytic activity is believed to be related to the formation of an active copper(III) species. The transition point between low and high pH as a function of cyanide and copper concentrations is discussed. Bulk electrolysis of a copper cyanide solution at 0.90 V oxidized most of the cyanide to cyanate. Prolonged electrolysis further oxidized the cyanate to nitrate. The copper oxide film is found to be catalytic, capable of electro-oxidizing hydroxide to oxygen and cyanate to nitrate. © 2002 Published by Elsevier Science Ltd.

Keywords: Cyanide oxidation; Copper complexes; Hydroxide ions; Copper oxide and nitrate

1. Introduction

Cyanide chemistry is usefully applied in gold mining, electroplating and metal finishing industries [1]. This, however, results in the need for treating large quantities of metal cyanide wastewater. In particular, those of the mining industry present a challenge because of their large volume and low concentration. The traditional method involves holding the solutions in large lagoons to allow the slow breakdown of the cyanide [2]. Once the cyanide is destroyed, the metal ions precipitate as hydroxides and the supernatant can be neutralized and discharged. This storage of large quantities of wastewater represents a cost both in terms of infrastructure and in terms of potential liability in the event of an accidental release [3].

Many alternative methods have been proposed, with two gaining some acceptance. Both approaches require copper cyanide complexes for catalysis, though the amount that must be added varies (one factor being the presence of significant amounts of copper in the wastewater from many gold mines). The first method is

the Inco SO_2 –air process [4,5]. This involves using SO_3^{2-} , which reacts together with oxygen and copper cyanide complexes resulting in cyanide oxidation and, in the presence of sufficient base, the formation of cyanate. While this process works well, it requires careful process control to keep the chemistry in its optimum balance. At the end of the reaction, copper precipitates out as copper hydroxide.

The second approach involves using hydrogen peroxide to oxidize copper cyanide complexes, leading to the formation of cyanate [6]. The peroxide reaction has two distinct phases. Initially, peroxide reacts with the $[\text{Cu}(\text{CN})_3]^{2-}$ complex producing cyanate with the overall reaction as shown in equation 1.

The $[\text{Cu}(\text{CN})_2]^-$ produced quickly reacts with free cyanide regenerating the $[\text{Cu}(\text{CN})_3]^{2-}$ complex. Once the free cyanide is consumed the reaction changes with the development of a yellowish color (with a broad absorption around 360 nm). The color is believed to be related to a copper(III) species. Such species were also obtained by reacting copper sulfate with hydrogen peroxide with no cyanide present [6], and have been

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reported for copper(II) perchlorate reacting with hypochloride and hypobromide [7].

The reaction of the second phase results in the destruction of the remaining cyanide, leading to the precipitation of the copper. However, the complex also catalyzes the evolution of oxygen by the decomposition of peroxide. The copper precipitate is reported to be copper hydroxide [6], though the authors describe the precipitate as light green at pH 8 but brown at pH 12, indicating the possible presence of copper oxide at the higher pH.

Overall, the peroxide process results in the very rapid oxidation of free cyanide with a rate that increases with higher copper concentrations. Unfortunately, as the free cyanide concentration decreases and the yellowish complex forms, the competing reaction involving the copper catalyzed decomposition of hydrogen peroxide begins to dominate [6]. Thus, while a higher concentration of copper increases the initial rate of cyanide destruction, it results in excessive hydrogen peroxide consumption in the later stages of the treatment. Therefore, designers must compromise between a rapid treatment rate (allowing a smaller reactor size) and efficient use of the hydrogen peroxide reagent.

Electrochemical oxidation for cyanide destruction has been demonstrated by several research groups [8–17]. While electrochemistry would be expected to require a higher capital cost, it should, by avoiding consumption of chemicals, be able to offer a lower operating cost. However, for system optimization and for accurate estimation of equipment and operating costs, a careful and quantitative understanding of the overall electrochemical process is required.

The electrochemical oxidation of cyanide to cyanate is also catalyzed by copper complexes. The various possible copper cyanide complexes and their equilibrium constants [18,19] are listed below:

The overall reaction for the oxidation of cyanide to cyanate is given by:

The mechanism for cyanide oxidation in the presence of copper has been suggested in the literature to be [10,20]:

The copper(II) complex, $[\text{Cu}_2(\text{CN})_6]^{2-}$, decomposes to release cyanogen and $[\text{Cu}(\text{CN})_2]^-$.

where the $[\text{Cu}(\text{CN})_2]^-$ can then combine with free cyanide to regenerate $[\text{Cu}(\text{CN})_3]^{2-}$ (equation 4). It is also thought that $[\text{Cu}(\text{CN})_4]^{3-}$ reacts by a similar route, which would require the loss of a cyanide ligand from the complex before forming $[\text{Cu}_2(\text{CN})_6]^{2-}$, however the exact steps remain to be determined. This mechanism has been considered as a solution reaction [20], though others feel that the predominant path involves a surface adsorbed intermediate [10]. This would not be surprising because the anionic nature of the possible intermediates. The potential dependent adsorption of some anionic copper cyanide complexes has been reported elsewhere [21].

The cyanogen produced then reacts with hydroxide to produce cyanate. This reaction has been studied by Margerum and coworkers [22] and is reported to occur by two parallel routes, with the distribution sometimes influenced by other anions in solutions. One route is a single-step reaction while the other involves a formamide intermediate [22].

and

These reactions can occur either close to the electrode or, if insufficient hydroxide is available, after diffusing out into the bulk of the solution.

In other papers, where a high copper and hydroxide concentrations were studied, a black deposit, identified as copper oxide (CuO), was formed at the anode [8,9,15] (with some copper hydroxide also associated with the film) [24]. This deposit was found to act as a heterogeneous catalyst for cyanide oxidation [8] and the oxidation of a range of organic compounds [24]. It was hypothesized [8,14] that a surface copper(III) intermediate was involved. Work investigating the electrochemistry of copper in alkaline solutions has shown the presence of Cu^{3+} at around 0.65 V versus Hg/HgO using a RRDE [25], related to a voltammetric

wave observed just before the onset of oxygen evolution [8,26].

In the work of Wels and Johnson [8], a charging wave at a copper oxide electrode attributed to oxidation of copper(II) to copper(III) was measured at 1 V min^{-1} in a sodium sulfate–sodium hydroxide solution at pH 12. This broad voltammetric wave (indicative of some lateral repulsion between the species being formed) started around 0.1 V versus SCE and increased in a steady manner until the onset of oxygen evolution at 0.8 V versus SCE. The intensity of the wave was also roughly proportional to the sweep rate, as would be expected for a surface reaction. In the presence of cyanide, a catalytic oxidation wave was observed, starting around 0.2 V versus SCE. A mass-transfer-controlled current plateau was observed corresponding to a cyanide diffusion coefficient of $1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, and the starting potential of the oxidation wave decreased in the presence of hydroxide.

As might be expected because of the complex chemistry, previous work on treatment of cyanide containing wastewater has reported different efficiencies and mechanisms, depending on the conditions used (such as pH and concentrations of cyanide and copper, as well as cell designs and operating conditions). It is therefore the goal of the present work to systematically investigate the effects of cyanide, copper, and hydroxide in the concentration ranges typically encountered in mining effluent. It is hoped by doing so to better clarify and quantify what is known about the copper-cyanide chemistry and to indicate what remains to be understood.

2. Experimental

The chemicals, CuCN (99.99%) and NaCN (97.9%), were obtained from Aldrich and used without further purification. Standardized 1.000 N sodium hydroxide and $18 \text{ M}\Omega \text{ cm}$ ultrapure water were used to prepare all solutions. The supporting electrolyte was 0.1 M sodium sulfate (BDH analytical reagent grade).

A conventional three-electrode electrochemical cell was used for all experiments. Glassy carbon, platinum and stainless steel 316 with surface areas of 0.196 cm^2 were used as working electrodes. Rotating disk electrode (RDE) experiments were controlled by the EG&G PARC Model 616 RDE apparatus. The auxiliary electrode was platinum gauze. Electrode potentials are reported versus a Hg/HgO/0.1 M NaOH reference electrode (Radiometer Analytical model XR-430). Unless otherwise stated, the scan rate was 2 mV s^{-1} . All electrochemical measurements were performed with a Solartron 1287 Interface. When IR interrupt was applied, the off time was set at 30 μs with an ON–OFF ratio of 200.

A beaker cell (running in batch mode) was used for bulk electrolysis of copper cyanide solutions. The working electrode was a platinized titanium disk (5.1 cm^2) mounted in a cell holder (similar to the EG&G K0105). The auxiliary electrode was a stainless steel 316 gauze connected to a platinum wire. In a typical experiment, 150 ml of the copper cyanide solution was electrolyzed with constant stirring.

Films were formed on the electrodes after some experiments. To obtain reproducible results, the electrodes were cleaned between experiments by rinsing with 10–15% nitric acid, followed by pure water, then polishing with $0.05 \mu\text{m}$ alumina using a Buehler micro-cloth. Following polishing, the electrode was soaked in 10–15% nitric acid for about 5 min, then rinsed with pure water and sonicated for 1 min.

The composition of the copper cyanide solution was analyzed by reversed-phase ion-interaction HPLC and cyanide ion-selective electrode. The HPLC technique was modified from the method described by Fagan et al. [27]. The stationary phase was a 15 cm Supelcosil LC-18-DB from Supelco. The mobile phase consisted of an ion-pairing agent (tetrabutylammonium hydrogen sulfate), a buffer (phosphate salts), 10 mM potassium cyanide and 200 ml of acetonitrile per litre. The ion-pairing agent and phosphate buffer were obtained as a prepared mixture (IPC-A) from Alltech or Waters. The pH of the mobile phase was adjusted to 7.3–7.4 by adding phosphoric acid. The cyanide in the mobile phase stabilizes the metal-cyanide complexes during chromatography. This method allowed analysis of copper cyanide, cyanate, and nitrate. Random testing of the copper cyanide solutions by atomic absorption spectroscopy yielded the same results within experimental error.

The cyanide concentration was measured using an Orion 9606 combination cyanide ion selective electrode (ISE). Samples (0.1 ml) were added into identical glass vial and stir bar sets containing the 6 ml of 0.5 M NaOH. To provide uniform mass transport, the electrode was inserted in the same position in each vial, and the sample agitated throughout the measurement with a magnetic stirrer set at a controlled stir rate. The electrode was calibrated before and after each set of samples using solutions made with standardized 1000 ppm cyanide solution from Labchem Inc.

The total cyanide concentration was estimated from the copper concentration and the cyanide concentration measured using the ISE. The ISE works by measuring the dissolution current for silver iodide in the presence of free cyanide. This results in a local displacement of the copper cyanide equilibria, leading to partial dissociation of the copper cyanide complexes, releasing additional cyanide. This introduces an additional factor in the ISE reading that depends on the amount of copper present and its degree of dissociation. This

degree of dissociation was estimated using a semi-empirical approach based on a method described previously [28]. This allows the total cyanide ($[\text{CN}^-]_{\text{T}}$) to be estimated using the ISE reading ($[\text{CN}^-]_{\text{ISE}}$), the copper concentration ($[\text{Cu}]_{\text{T}}$), and a correction factor associated with the amount of copper (ε):

$$[\text{CN}^-]_{\text{T}} = [\text{CN}^-]_{\text{ISE}} + [\text{Cu}]_{\text{T}}\varepsilon \quad (15)$$

where:

$$\varepsilon = \frac{1.96\alpha_1 \text{CN}_{\text{ISE}} + 1.0\alpha_2 - \frac{3}{2\text{CN}_{\text{ISE}}}}{\alpha_1 \text{CN}_{\text{ISE}} + \alpha_2 + \frac{1}{\text{CN}_{\text{ISE}}}}$$

and α_1 and α_2 are empirical constants found in this work to be equal to $1.6 \times 10^3 \text{ mM}^{-2}$ and $2.1 \times 10^1 \text{ mM}^{-1}$, respectively.

The difference between total cyanide and measured cyanide, normalized for the copper concentration, (ε), is shown in Fig. 1 for a series of standard solutions measured at various times over the course of this work. This difference is basically the average number of cyanide ligands held per copper, and thus unavailable to be measured by the ISE. The fit obtained with Eq. (15) is also plotted and gives a standard error in the estimate of ε of 0.28. Further verification of this approach was obtained by random testing of various experimental samples for total cyanide using total cyanide distillation, which gave comparable results, within experimental error.

Fig. 1. Calibration curve for the correction factor for the cyanide ISE with copper present, showing the fit obtained with the α_1 and α_2 empirical constants.

3. Results and discussion

3.1. Effects of copper and hydroxide concentrations on cyanide oxidation

In Fig. 2, a series of voltammograms is plotted showing the effect of copper and of hydroxide on the electrochemical response. With a cyanide solution, no visible oxidation wave can be seen at the glassy carbon anode up to the onset of oxygen evolution. With 1.7 mM of copper in solution, however, an oxidation wave becomes visible starting around 0.3 V and reaching a plateau around 5 mA cm^{-2} . If sufficient hydroxide is added to ensure complete oxidation of the cyanide, an increase in the oxidation wave is visible starting around 0.62 V and rapidly increasing starting at 0.68 V. This increased activity compared with the low hydroxide case continues on the return sweep.

The effect of hydroxide concentration can more clearly be seen in the polarization curves shown in Fig. 3. Several distinct regions can be observed. The initial region, up to about 2 mA cm^{-2} , corresponds to oxidation of the copper cyanide complex(es) at the glassy carbon electrode. This reaction, as mentioned in the introduction, is believed to occur through the oxidation of $[\text{Cu}(\text{CN})_3]^{2-}$ and/or $[\text{Cu}(\text{CN})_4]^{3-}$. The currents in this region were found to be somewhat irreproducible and the Tafel slopes were typically around 140–200 mV per decade. Such irreproducibility tends to be the characteristic of a surface sensitive, heterogeneous reaction, thus supporting the results of Hofseth and Chapman [10,11]. The Tafel slope is indicative of a rate determining step involving the initial electron transfer.

Fig. 2. Voltammetric response of 6.8 mM cyanide solution at a glassy carbon RDE at 2500 rpm, 2 mV s^{-1} , and 0.1 M Na_2SO_4 . (a) with 1 mM NaOH, (b) with 1.7 mM Cu^+ and 1 mM NaOH, and (c) with 1.7 mM Cu^+ and 16 mM NaOH.

Fig. 3. Polarization curves showing the effect of hydroxide. Glassy carbon RDE at 2500 rpm and 2 mV s^{-1} . Solutions contain 1.7 mM Cu^+ , 6.8 mM CN^- , $0.1 \text{ M Na}_2\text{SO}_4$ with (a) 1 mM OH^- , (b) 6 mM OH^- , (c) 11 mM OH^- , (d) 16 mM OH^- , and (e) 21 mM OH^- . The estimated limiting current values for $[\text{Cu}(\text{CN})_3]^{2-}$, reactable ($[\text{Cu}(\text{CN})_3]^{2-} + \text{free cyanide}$), and total destruction (to cyanate and copper oxide) are shown for reference.

At the end of this initial region the data for the solution containing only 1 mM of hydroxide approaches a limiting current, while the other curves show a very different behavior. When sufficient hydroxide is present the polarization curve shows a large current increase around $0.7\text{--}0.75 \text{ V}$. In some experiments (shown later), this current increase was observed to be very abrupt and is therefore believed to be related to an autocatalytic process. After this transition the currents increase more slowly, reaching a higher final value for higher hydroxide concentrations.

After such a polarization sweep in a solution with these higher hydroxide concentrations, the electrode was covered with a black film. In a separate experiment, the black film was scraped off and analyzed by XPS. The result matched CuO as reported in the XPS handbook and is consistent with the literature [8,15]. Though it should be mentioned that in recent work by Casella and Gatta [24], they were able to quickly transfer the film into an XPS and detected $\text{Cu}(\text{OH})_2$ as well as CuO at the film surface.

We can further analyze the polarization curves by looking at the expected limiting currents for various possible reactions. Calculating the limiting currents for the cyanide system is complicated due to the equilibria that exist between the various copper cyanide complexes, which will shift within the concentration gradient near the electrode surface. Further, the subsequent diffusion and reaction of cyanogen with hydroxide (equations 10–14) can affect the extent of oxidation of the cyanide. For low hydroxide concentrations, where the reaction will proceed slowly, most of the cyanogen will diffuse out to the bulk and thus only one electron is transferred from each reacted cyanide (equations 7–9) ($z_{\text{eff}} = 1 \text{ eq. mol}^{-1}$). At higher hydroxide concentrations, more of the cyanogen will be decomposed before

diffusing far from the electrode, thus releasing free cyanide close to the electrode for further oxidation. The upper limit for z_{eff} will then be 2 eq. mol^{-1} if complete conversion of cyanide to cyanate occurs (equation 6). The z_{eff} values will also change with the diffusion distance, since with increasing RDE rotation rates (thus smaller diffusion distances) more cyanogen is lost into solution and a limiting current corresponding to a z_{eff} of closer to 1 eq. mole^{-1} would result. Thus assuming a z_{eff} of 2 eq. mol^{-1} can only be done at higher pHs and/or slower rotation rates. An approach to estimate these effects has been developed by Hofseth and Chapman [11], though it does not include the full complexity of the reaction mechanism presented earlier [22].

Using approximate z_{eff} values and the diffusion coefficients shown in Table 1, the currents corresponding to various degrees of oxidation of the cyanide species were estimated. The limiting current for the reactant, $[\text{Cu}(\text{CN})_3]^{2-}$, was calculated for a z_{eff} value of 1.5 eq. mol^{-1} (an average value to cover the $1\text{--}21 \text{ mM}$ hydroxide cases in Fig. 3). However, because free cyanide would quickly react with $[\text{Cu}(\text{CN})_2]^-$ produced at the electrode to regenerate $[\text{Cu}(\text{CN})_3]^{2-}$, a second limiting current based on the sum of the $[\text{Cu}(\text{CN})_3]^{2-}$ and CN^- fluxes was also calculated for both z_{eff} values (labeled as the reactable cyanide current in Fig. 3). This represents the limiting current when $[\text{Cu}(\text{CN})_2]^-$ is electrochemically inactive, and is similar to the first stage of oxidation with peroxide. It is also interesting to note that at the reactable cyanide limiting current, $[\text{Cu}(\text{CN})_2]^-$ is the primary species at the electrode surface. Finally, a total destruction limiting current is estimated using the flux for the bulk concentration of free cyanide with a z_{eff} of 2 eq. mol^{-1} plus the flux for the bulk concentration of $[\text{Cu}(\text{CN})_3]^{2-}$ and a z_{eff} of 7 eq. mol^{-1} . This represents the maximum possible current for the complete conversion of the cyanide species to cyanate and copper oxide.

Referring to Fig. 3, it can be seen that, other than the 1 mM case, the current increases smoothly (with no

Table 1
Diffusion coefficients used for estimating limiting currents

Species	Diffusion coefficient ($\text{cm}^2 \text{ s}^{-1}$)	Source
Hydroxide	5.26×10^{-5}	CRC handbook [22]
Cyanide	2.08×10^{-5}	CRC handbook [22]
$[\text{Cu}(\text{CN})_4]^{3-}$	6.21×10^{-6}	Dudek and Fedkiw [29]
$[\text{Cu}(\text{CN})_3]^{2-}$	1.08×10^{-5}	Dudek and Fedkiw [29]
$[\text{Cu}(\text{CN})_2]^-$	1.43×10^{-5}	Dudek and Fedkiw [29]

deviation around the limiting current for $[\text{Cu}(\text{CN})_3]^{2-}$ up to about 0.65–0.75 V and then rapidly increases to around the limiting current for the total destruction of the cyanide species. Currents greater than this are expected to be due to the discharge of unreacted hydroxide ion to form oxygen (see below). Thus, one would expect that one requirement to achieve this enhanced activity for cyanide oxidation would be that the hydroxide limiting flux is sufficient to supply both the cyanide oxidation (equation 6) and the copper complex oxidation (equation 16). Thus approximately:

$$[\text{OH}^-] \geq \frac{2D_{\text{CN}^-}[\text{CN}^-] + 8D_{[\text{Cu}(\text{CN})_3]^{2-}}[\text{Cu}(\text{CN})_3]^{2-}}{D_{\text{OH}^-}} \quad (17)$$

(Note: for the RDE, the diffusion coefficients would be to the 2/3 power.)

Using the conditions for Fig. 3 (1.7 mM $[\text{Cu}(\text{CN})_3]^{2-}$, 1.7 mM for $[\text{CN}^-]$, at an RDE) this estimates a minimum required hydroxide concentration of about 6.5 mM to achieve rapid cyanide treatment. And, as can be seen in Fig. 3, the results for 6 mM hydroxide would thus be expected to yield a limiting current very close to that for complete cyanide destruction.

3.2. Characteristics of the copper oxide catalytic coating

The discharge of hydroxide ion is interesting because oxygen evolution was not visible in the background sweep with the glassy carbon electrode in the copper free solution (see Fig. 2). To investigate this, cyclic voltammetry experiments on glassy carbon and a copper oxide modified glassy carbon electrode were performed in several concentrations of sodium hydroxide containing 0.1 M Na_2SO_4 . The copper-oxide-modified glassy carbon electrode was prepared by electrolyzing a glassy carbon electrode for 3 min at 0.9 V at a rotation rate of 900 rpm in a solution containing 1 mM copper, 4 mM cyanide and 21 mM NaOH. After rinsing with distilled water, the electrode was transferred to solutions with various concentrations of sodium hydroxide and 0.1 M Na_2SO_4 . The cyclic voltammograms of the electrolyte solutions containing 1–11 mM of hydroxide at the two electrodes are shown in Fig. 4. Oxidation peaks at 0.88 and 1.38 V are observed on the copper oxide coated glassy carbon electrode and the plain glassy carbon electrode, respectively. Similar experiments for hydroxide oxidation were also performed on platinum and a copper oxide modified platinum electrode. Oxidation peaks at 0.91 and 1.20 V are observed on the copper oxide modified platinum electrode and the plain platinum electrode, respectively. The oxidation potential of the copper oxide modified platinum electrode is similar to the copper oxide modified glassy carbon electrode, suggesting that the hydroxide oxidation originates on the copper oxide film. This implies that the current

Fig. 4. Cyclic voltammograms of CuO modified glassy carbon electrode and plain glassy carbon electrode in various concentrations (1–11 mM) of hydroxide and 0.1 M Na_2SO_4 at 10 mV s^{-1} .

observed in Fig. 3 starting around 0.75–0.85 V, which is in addition to the total cyanide destruction limiting current, is likely due to the oxidation of hydroxide ion. It further implies that, at that point in the polarization curve, copper oxide is present on the electrode surface.

Fig. 4 also shows an electrode charging current at the copper oxide coated electrode starting at 0.25 V and steadily increasing up to about 0.75 V. This charging wave retains its shape with various hydroxide concentrations and is similar in position and shape to results reported by others [8,24] which were attributed to the oxidation of copper(II) to copper(III). For copper in alkaline solution without cyanide present, the oxidation of copper(I) to copper(II) takes place at approximately -0.1 V versus SCE leading to the formation of $\text{Cu}(\text{OH})_2$ [30]. We have observed that for copper in 0.1 M Na_2SO_4 and 10 mM NaOH, the oxidation of copper(I) to copper(II) occurs at -0.04 V versus Hg/HgO/0.1 M NaOH (not shown). The further oxidation of copper(II) to copper(III) has been reported to occur around 0.65 V versus Hg–HgO [8,25,26]. Therefore, once the local cyanide concentration at the electrode surface is driven close to zero (currents greater than the total destruction line in Fig. 3), the stable form of copper at these potentials and with predominately hydroxide and oxygen available as ligands would be the +2 or +3 state. This is important because both the +2 and +3 states of copper can form a range of complexes [7,31] which could interact with cyanide and/or hydroxide, thus explaining the very high activity found for cyanide oxidation and oxygen evolution above 0.65–0.75 V.

As mentioned earlier, complexes of copper(III) have also been reported to be the active catalyst for the oxidation of copper cyanide solutions with hydrogen

peroxide. During our own tests, upon the addition of hydrogen peroxide to copper cyanide solutions, a yellow color was observed, which has been reported to be a copper(III) complex [6]. After completion of the reaction, a dark brown precipitate appears, corresponding to CuO. It is interesting to note that when copper sulfate is added to an alkaline solution, a light blue deposit of Cu(OH)₂ is formed, which converts to the dark brown CuO slowly, over a couple of days. This implies that decomposition of the copper(III) complex to CuO is faster than that of Cu(OH)₂. This is of interest because in the electrochemical case, CuO is observed to appear very rapidly on the electrode surface. This is in agreement with Casella and Gatta [24] who found that voltages in the range where copper(III) is expected, were required to form a CuO deposit on an electrode.

Polarization measurements were also carried out at various electrode rotation rates, with the results shown in Fig. 5. It can be seen that the initial currents (below 0.7 V) are random (i.e. do not correlate with the rotation rate). However, once the electrode activity increases (at around 0.7–0.8 V), the currents become dependent on the rotation rate. In Fig. 6, the currents measured at 0.8 V are plotted with the calculated current for the total destruction of the cyanide, and the currents at 1.0 V are plotted with the sum of total destruction of the cyanide plus the expected current for the oxidation of the remaining hydroxide to oxygen. The data at 0.8 V fit the estimated current for total destruction of the cyanide reasonably well. The data at 1.0 V, except for the 3600 rpm results, appear to follow the estimated curve. One reason for the lower than expected hydroxide current could be due to the lack of a true limiting current plateau at 1.0 V especially at higher rotation rates. The low activity of the electrode for the 3600 rpm experiment is believed to be due to some loss of the copper oxide coating at this rotation rate. This idea was supported by

Fig. 5. Polarization curves for copper-cyanide solution with 1.7 mM Cu⁺, 6.8 mM CN⁻, 17.9 mM hydroxide and 0.1 M Na₂SO₄ at a glassy carbon RDE at 2 mV s⁻¹. (a) 400 rpm, (b) 900 rpm, (c) 1600 rpm, and (d) 3600 rpm.

Fig. 6. Effect of rotation rate on current density with data extracted from Fig. 5.

a somewhat erratic current–voltage curve observed during the reverse sweep for the 3600 rpm experiment.

The effect of anodic materials was also tested with some typical results shown in Fig. 7. Both glassy carbon and platinum results show a very slow increase in current with a transition to higher activity occurring around 0.7–0.8 V, with the platinum showing a particularly abrupt transition. For stainless steel, the curve starts out with what appears to be a typical stainless steel passivation from 0.25 V up to about 0.6 V followed by breakdown of the passivation and the simultaneous onset of cyanide oxidation. It is also interesting to note that the stainless steel current at 1.0 V is lower and the activity on the back sweep was also lower. This could possibly be due to a less active copper oxide film caused by differences in the conductivity and/or the nucleation of the copper oxide film, or simply due

Fig. 7. Polarization curves of copper-cyanide solution containing 5.5 mM Cu⁺, 21.6 mM CN⁻, 20 mM hydroxide and 0.1 M Na₂SO₄ on rotating glassy carbon, platinum and stainless steel 316 electrodes at 2500 rpm.

to adhesion problems. In the work of Wels and Johnson [8], special care had to be taken in order to produce uniform and adherent films. In our work, coating adhesion problems were also encountered at high rotation rates (described earlier) and at high excess hydroxide concentrations, thought to be due, at least in part, to the higher rates of oxygen bubble evolution at 1.0 V with excess hydroxide. It was also noted that films formed at higher excess hydroxide concentrations were often rougher, leading in some cases to higher than expected limiting currents. Casella and Gatta [24] also reported problems obtaining a thick coating at higher potentials and pHs, which they thought was due to interference from oxygen evolution.

Steady-state voltammograms are shown in Fig. 8, recorded after previously cycling the glassy carbon five times at 10 mV s^{-1} using a balance of copper, cyanide, and hydroxide concentrations for stable copper oxide film formation (i.e. using equation 17, but without too much hydroxide to avoid excessive oxygen evolution). One interesting observation is the large cathodic peak visible on the negative going sweep, which generally seemed to increase and shift to more positive potentials with increasing copper concentration, though hydroxide concentration also had some effect on the height and shape of the peak. In the work of Wels and Johnson [8], where cyanide was oxidized at a pre-formed copper oxide coated electrode (i.e. without copper in solution) no such cathodic peaks were reported. We therefore believe that this peak is due to reduction of some copper species deposited during the prior anodic sweep.

Voltammetric curves for cyanide oxidation at pre-formed copper oxide coated electrodes reported by Wels and Johnson [8] show an anodic current starting around

Fig. 8. Voltammetric response of copper-cyanide solutions with 0.1 M Na_2SO_4 at a CuO modified glassy carbon RDE at 2500 rpm, (a) 1.0 mM Cu^+ , 4.1 mM CN^- and 5 mM hydroxide; (b) 2.8 mM Cu^+ , 10.8 mM CN^- and 15 mM hydroxide; and (c) 5.7 mM Cu^+ , 22.4 mM CN^- and 33 mM hydroxide.

0.25 V versus SCE at pH 12 (hence about 0.28 V versus Hg/HgO) reaching a limiting current plateau at about 0.4 V versus SCE (0.43 V Hg/HgO), which continued up to the beginning of oxygen evolution around 0.75 V versus SCE (0.78 V Hg/HgO). It can be seen in Fig. 8 that in the present work we also obtain a rapid rise in current around 0.25–0.35 V which begins to level off around 0.29–0.43 V, however no clear single limiting current plateau occurs, rather a slower and somewhat stepwise increase in current is observed. In the work of Wels and Johnson [8], the reaction was that of free cyanide at the copper oxide surface. In this work, the free cyanide is in equilibrium with the copper cyanide complexes, and so its reaction will cause dissociation of the complexes. However, because of the finite rate of dissociation of the copper cyanide complexes (the dissociation rate of $[\text{Cu}(\text{CN})_3]^{2-}$ would be 2×10^5 times slower than the association rate ($k_r = k_f/K_{\text{eq}}$) (see equation 4), an inflection in the current increase might occur around the simple free cyanide limiting current. Thus the multi-step plateau might be related to the progressive dissociation or reaction of the various copper complexes. A second possibility for the multi-step plateau might be due to different surface copper complexes, which would change with the electrode potential and the balance of chemical species at the electrode surface.

It is also unclear if the cyanide oxidation mechanism is significantly different at the copper oxide surface. Wels and Johnson [8] used a Levich plot of the limiting current and a z_{eff} of 2 eq. mol^{-1} to calculate a diffusion coefficient for cyanide of $1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, somewhat lower than the literature value of $2.08 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [23]. The z_{eff} of 2 eq. mol^{-1} was determined from preparative electrolysis, which would not show the effect of the finite decomposition rate of cyanogen. If cyanogen is also produced at the copper oxide electrode, the apparent z_{eff} could be lower than 2 eq. mol^{-1} , resulting in the reported under-prediction of the diffusion coefficient.

The presence of copper oxide at the electrode surface also affects the oxidation of the copper cyanide complexes. It was found during separate preparative electrolysis experiments, carried out as described in the preparative electrolysis section but using 0.5 V (hence in the plateau region), no copper oxide was formed at a platinized titanium electrode. However, if the platinized titanium was previously coated with a deposit of copper oxide, the deposit would thicken. Thus for the copper cyanide complexes, a different reaction mechanism may occur at the copper-oxide-coated electrode. Obviously further work is needed to understand the reaction mechanisms for cyanide and copper cyanide at the copper oxide coated anode.

The chemical oxidation of cyanide by copper oxide was observed to be surprisingly slow. During some

experiments pieces of the black CuO coating, which sometimes fell off the anode, were found to be quite stable in cyanide solution over a period of days. In comparison, freshly precipitated Cu(OH)₂ would dissolve when placed in a cyanide solution over a period of minutes. Also, CuSO₄ added directly to a cyanide solution formed a blue color that rapidly disappeared as it dissolved (as also reported by Beattie and Polyblank [6]). Thus, copper(II), if present as a hydrated complex or a dissolved ion, can be active for the chemical oxidation of cyanide, while the dry oxide does not appear to be active.

Other information about the state of the copper oxide surface comes from the voltammetric sweeps. The onset of catalytic cyanide oxidation at the copper oxide coated electrode was found to be related to a reversible process, as evidenced by a small cathodic current that begins to flow at potentials cathodic to cyanide oxidation (see Fig. 9). This cathodic current is also visible in the work of Wels and Johnson [8], and similar to our work, only appears in the presence of cyanide (it is not visible in Fig. 4). While the reduction of copper(II) (CuO or Cu(OH)₂) to Cu₂O occurs at far more negative potentials (−0.26 and −0.21 V, respectively [32]), the reduction of copper(II) species to soluble cyanides might be expected to occur around these potentials, with the hydrated form more likely to interact with cyanide (as discussed above), e.g.

which, for [OH[−]] = 17.9 mM, [CN[−]] = 1.7 mM, and [Cu(CN)₂[−]] = 1 × 10^{−6} M would have an equilibrium potential of 0.47 V versus Hg–HgO (calculated using chemical potentials from reference [34]). It was also

noted that the cathodic current is independent of electrode rotation rates, indicating that it is not mass transfer limited. Further the magnitude of the current does not continuously increase as the potential becomes more cathodic, indicating that a limited amount of material is available to be reduced. This cathodic current may therefore be due to the reduction of a small amount of hydrated copper(II) present at the electrode surface (such hydrated copper(II) at the surface of the copper oxide deposit has been detected by others using XPS [24]).

Thus, the active species leading to the enhanced oxidation of cyanide at the copper oxide coated electrode could be a copper(III) complex, a copper(II) complex, or a combination of both, with the surface coverages depending on the potential and the local concentrations of various species at the electrode surface (this effect of local concentrations possibly being analogous to the changes in mechanism from copper(II) to copper(III) catalysis observed with hydrogen peroxide treatment, which depends on the amount of free cyanide versus hydroxide, as presented in the introduction). The onset of cyanide oxidation could then be related to the presence of a small amount of copper(III) (as indicated by the start of the pseudo-capacitance above 0.25 V in Fig. 4) and/or to the ability to regenerate some copper(II) hydroxide–cyanide species from its copper(I) form. More work is obviously required to fully determine the mechanism of the catalysis by the copper oxide coated electrode.

3.3. Cyanide oxidation at low hydroxide concentration

Experiments were also carried out to study the cyanide oxidation under conditions where there was insufficient hydroxide for the formation of a copper oxide coating. Under these conditions, the primary product of the cyanide oxidation will be cyanogen (Equation 9). Typical voltammograms under these conditions are shown in Fig. 10. The current rises slowly and smoothly eventually approaching a limiting current above 0.9 V. As was discussed with Fig. 3, this slow current increase corresponds to a Tafel slope of greater than 120 mV per decade and hence an initial electron transfer rate determining step. Hofseth and Chapman [11] have reported a transfer coefficient of about 0.36. The voltammograms also show a large and very broad hysteresis loop, which becomes larger with increasing copper concentration (also visible in Fig. 11). (Though please note that an increasing copper concentration also implies a lower OH[−]/Cu⁺ ratio). As the tests were done at a RDE the hysteresis must involve a surface species with a broad peak width characteristic of adsorbed species with strong lateral repulsion. It was also observed in other tests that the magnitude of the

Fig. 9. Voltammetric response showing a blow-up of the cathodic current on the reverse sweep of a copper–cyanide solution containing 1.7 mM Cu⁺, 6.8 mM CN[−], 17.9 mM hydroxide and 0.1 M Na₂SO₄ at a CuO modified glassy carbon RDE. (a) 400 rpm, (b) 900 rpm, (c) 2500 rpm, and (d) 3600 rpm.

Fig. 10. Voltammetric response of a copper-cyanide solution containing 6.8 mM CN^- , 1 mM hydroxide, 0.1 M Na_2SO_4 and various copper concentrations at a glassy carbon RDE at 2500 rpm, (a) 0.0688 mM Cu^+ ; (b) 0.344 mM Cu^+ ; (c) 1.03 mM Cu^+ ; and (d) 1.72 mM Cu^+ .

Fig. 11. The effect of copper concentration on the current density at various potentials; measured as described for Fig. 10.

hysteresis was independent of sweep rate, indicative of a chemical rate determining step.

It was also observed that the limiting currents increased with decreasing copper concentration until around 0.344 mM copper, then rapidly decreased. The currents measured at 0.8, 0.9 and 1.0 V are plotted in Fig. 11 along with the estimated contributions of various species to the total current. Due to the very low hydroxide concentration near the electrode under these conditions the limiting current for the copper cyanide complexes was calculated using $[\text{Cu}(\text{CN})_3]^{2-}$ with a z_{eff} of 1.0 eq. mol^{-1} and $[\text{Cu}(\text{CN})_4]^{3-}$ with a z_{eff} of 2.0 eq. mol^{-1} (thus reacting to produce $[\text{Cu}(\text{CN})_2]^-$) (note that $[\text{Cu}(\text{CN})_4]^{3-}$ was included in these calculations because of the higher free cyanide levels in some of

these experiments). If the limiting current for free cyanide (also with a z_{eff} of 1.0 eq. mol^{-1}) is added to this curve, a reasonably good fit is obtained. This corresponds to the reactable cyanide calculation used earlier, which represents the limiting current assuming $[\text{Cu}(\text{CN})_2]^-$ to be electrochemically inactive, thus similar to the first stage of oxidation with peroxide.

Assuming that $[\text{Cu}(\text{CN})_2]^-$ could react would result in a large over-estimation of the limiting current. It is speculated that $[\text{Cu}(\text{CN})_2]^-$ can not be easily oxidized under these conditions because additional ligands might be needed to stabilize the square planar copper(II), and under these reaction conditions the local hydroxide concentration at the electrode surface will be depleted. (Copper(II) compounds with hydroxide ligands have been described in detail by Margerum and co-workers [7,22]). It is possible, however, that some partial oxidation of the $[\text{Cu}(\text{CN})_2]^-$ to an adsorbed intermediate (without sufficient hydroxide to complete the reaction to copper oxide) may be responsible for the observed hysteresis.

Considering Fig. 11, it can be seen that decreasing the copper concentration results in more of the total cyanide being available as free cyanide. This increases the amount of reactable cyanide if cyanide tied up as $[\text{Cu}(\text{CN})_2]^-$ is unreactive. A second reason for the increasing current is the higher diffusion coefficient (see Table 1) of free cyanide versus $[\text{Cu}(\text{CN})_3]^{2-}$ (thus underlining the importance of considering the various copper cyanide species when estimating the limiting current). However, below a copper concentration of about 0.344 mM, there is not sufficient copper to properly catalyze the oxidation reaction (equations 7–9). Thus, the current for the 0.0688 mM copper experiment starts at a more positive potential (see Fig. 10) and has not reached a mass transport limited plateau by 1.0 V.

3.4. Bulk electrolysis

Bulk electrolysis was also carried out with copper cyanide solutions. Experiments were performed with a platinized titanium anode at 0.90 V with a solution containing 2.5 mM copper, 9.8 mM cyanide, 20 mM sodium hydroxide and 0.1 M sodium sulfate. The pH of the solution dropped from 12.1 to 9.9 over the course of the experiment. Samples were taken and analyzed by HPLC and ISE; the results are shown in Fig. 12. The concentration of copper and total cyanide in the solution decreases gradually while the concentration of cyanate increases. Once the cyanide has been mostly reacted the cyanate begins to oxidize producing nitrate. A current efficiency of 63% was obtained for a two-third removal of cyanide assuming two electrons are required to oxidize one cyanide. Massive oxygen evolution was observed at the beginning of the electrolysis, explaining

Fig. 12. Bulk electrolysis of copper-cyanide solution containing 2.5 mM Cu^+ , 9.8 mM CN^- , 20 mM OH^- and 0.1 M Na_2SO_4 at 0.9 V vs. Hg–HgO using a platinized titanium anode.

the lower than expected current efficiency. One should note that the final concentration of cyanate and nitrate did not add up to the starting concentration of cyanide. As discussed below, cyanate could be oxidized to nitrogen and the hydrolysis of cyanate to ammonia can occur over time (though the latter is favored at pH values below 7). Though nitrogen and ammonia were not analyzed (and no odor of ammonia was noticed), it is reasonable to expect that they are possible end products of cyanide oxidation.

Experiments with the same procedure were also carried out at 0.70 V and the results were somewhat different. The formation of the copper oxide film was not instantaneous and the maximum current density was reached when the electrode was completely covered by the black film. The reaction rate of cyanide destruction was slower at the lower potential. Nonetheless, there was some improvement in the current efficiency. Unlike the electrolysis at 0.90 V, exhaustive electrolysis of the copper cyanide solution at 0.70 V gave undetectable or only trace amounts of nitrate.

While previous work in the literature has discussed the electrochemical oxidation of cyanide to cyanate, no work was found mentioning the electrochemical oxidation of cyanate to nitrate. However, the photocatalytic oxidation of cyanate over TiO_2 to nitrate has been reported in the literature [33]. We have demonstrated that cyanate can also be electrochemically oxidized to nitrate.

To better understand the oxidation of cyanate to nitrate, further experiments were performed. On platinized titanium, 20 mM of sodium cyanate, 10 mM of sodium hydroxide and 0.1 M of sodium sulfate was electrolyzed at 0.95 V for 9 h. The solution was analyzed by HPLC and no nitrate was detected at the end of the electrolysis. These results prompted us to investigate the

catalytic activity of the copper oxide film. A copper oxide modified platinized titanium electrode was prepared by electrolyzing in a copper cyanide solution containing 5.5 mM of copper, 22.0 mM of cyanide, 20 mM of sodium hydroxide and 0.1 M sodium sulfate at 0.90 V for 2.5 min. After rinsing the black copper oxide film with pure water, the copper oxide modified electrode was used for a second electrolysis of a solution containing 20 mM of sodium cyanate, 10 mM of sodium hydroxide and 0.1 M of sodium sulfate. After electrolyzing at 0.95 V for 9 h, 25% of cyanate was oxidized of which 50% was converted to nitrate. Assuming cyanate is electrochemically oxidized to nitrate, eight electrons are required per cyanate ion.

However, this yields an overall current efficiency of 126%. In addition, some of the current may be used for oxygen evolution since some gas bubbles were observed at the beginning of the electrolysis. Thus, the reaction is likely to be more complicated.

Since only half of the cyanate is oxidized to nitrate, the other half of the cyanate may be converted to ammonia and/or nitrite. The hydrolysis of cyanate to ammonium does not involve any electron transfer process. The oxidation of cyanate to nitrite involves six electrons per cyanate and the nitrite can then be oxidized to nitrate by the dissolved oxygen in the solution, and thus could explain the observed current efficiency.

4. Conclusions

The reactions involved in cyanide oxidation at low and high hydroxide concentrations are very different. At low hydroxide concentrations, no CuO film was observed on the electrode surface. The results under these conditions were consistent with catalysis by surface adsorbed species of $[\text{Cu}(\text{CN})_3]^{2-}$ (and possibly $[\text{Cu}(\text{CN})_4]^{3-}$), with an electron transfer rate determining step.

At high hydroxide concentrations, autocatalytic reactions occur, quite likely involving a copper(III) species, resulting in a CuO film on the electrode. Under these conditions, the oxidation of cyanide and copper cyanide complexes is rapid and complete at around 0.75 V and above. The CuO -coated electrode is also catalytic for oxygen evolution, starting around 0.75 V. Thus precise potential control is required to obtain rapid cyanide oxidation combined with good current efficiency. This rapid cyanide oxidation is thought to be catalyzed by copper(II) complexes and/or copper(III) complexes. With increasing potential, the current for cyanide oxidation increases in a series of steps to the limiting current for the complete oxidation of cyanide and copper cyanide complexes. The steps may be related to

the various catalytic copper complexes and/or the finite rate of dissociation of the copper cyanide complexes and their different oxidation potentials. The concentrations of the various catalytic copper complexes may depend on the potential as well as on the local concentrations of ligands such as: CN^- , OH^- , and OCN^- (in order of decreasing ligand field strength) at the electrode surface.

Bulk electrolysis of copper cyanide solutions resulted in the oxidation of cyanide to cyanate, with 63% Faradaic efficiency. With further oxidation cyanate was successfully oxidized to nitrate (thus minimizing the formation of toxic ammonia from the hydrolysis of cyanate). This oxidation of cyanate to nitrate did not occur on platinized titanium unless it was coated with copper oxide. This builds upon the work of others who have shown that copper oxide electrodes are catalytic for oxidizing cyanide to cyanate [8], and for oxidizing of a range of organic compounds [24,26].

Our results confirm that cyanide containing mining wastewater can be treated electrochemically, but also show the importance of controlling the solution pH and the electrode potential. This has implications for three-dimensional electrodes (the type most likely used for practical applications) where voltage variations can occur, especially in low conductivity solutions. Indeed, preliminary work with three-dimensional electrodes has found that control of voltage variations is important not only to obtain good current efficiencies, but also to obtain an even deposit of the catalytic CuO coating and thus to get even electrode performance. However, even though precise potential control is required for electrochemical treatment, such control is possible with careful design. Thus, electrochemical treatment can achieve rapid initial (possibly copper(III) catalyzed) reaction rates like the hydrogen peroxide treatment. In addition, because of the ability to precisely control the oxidation potential, electrochemistry can continue to remove cyanide to low concentrations with good efficiency, this being an advantage versus the peroxide treatment method.

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