volves now more defining conditions. Since the evidence for tristability is not conclusive at 208 °C, we do not pursue this avenue.

Nomenclature

a = stoichiometric coefficient
a_v = surface-to-volume ratio
C_i, C_{bi} = surface and bulk concentration, vol %
Da = Damkohler number
E_i/R = activation energy, K
F = steady-state function
h = heat-transfer coefficient
K_i = adsorption equilibrium coefficient
k, k_0 = reaction rate constant and preexponential factor, respectively
k_c = mass-transfer coefficient
l = apparent reaction order
m = order of reaction
n = inhibition order
Q = heat input by oven
r = reaction rate
T_a, T_b, T_s = ambient, apparent bulk, and solid temperature, respectively
x = degree of conversion

Greek Symbols

α = dimensionless exothermicity, $C_{b1}E_1\lambda/RT_s^2$
$(-\Delta H)$ = heat of reaction
λ = adiabatic temperature rise per 1 vol % C_{b1}

Subscript

i = species i

Registry No. Pt, 7440-06-4; C_2H_4, 74-85-1.

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The Effect of Copper and Iron Complexation on Removal of Cyanide by Ozone

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Oxidation of cyanide by ozone in basic aqueous solution was studied in the absence and presence of copper and iron. Free cyanide was oxidized via a fast reaction under mass-transfer-limited conditions. Copper catalyzed the oxidation of cyanide further by entering into an oxidation–reduction reaction. Oxidation of cyanide consumed equal moles of ozone and produced equal moles of cyanate. Upon prolonged ozonation, cyanate was converted to carbon dioxide. Complexation of cyanide with iron hindered the oxidation reaction. Under the experimental conditions, oxidation of each mole of iron-complexed cyanide to carbon dioxide required the consumption of more than 30 mol of ozone. Cyanate was not detected during ozonation of iron–cyanide complex.

Complete destruction of free cyanide ion in aqueous solution has been reported unanimously by numerous researchers (Gurol and Bremen, 1985; Rowley and Otto, 1980; Zeelvalkink et al., 1979; Matsuda et al., 1975a,b; Balyanskii et al., 1972; Sondak and Dodge, 1961a,b; Khandelwal et al., 1959; Selm, 1959; Walker and Zabban, 1953). However, there is disagreement as to the effects of metal complexation of cyanide on the reaction rate. For example, copper as Cu(II) was found to catalyze the oxidation of cyanide (Matsuda et al., 1975a,b; Khandelwal et al., 1959). It was believed that Cu^{++} formed an oxide with ozone; subsequently, Cu^{++} was regenerated by a reaction of the oxide with cyanide (Khandelwal et al., 1959). Matsuda et al. (1975a,b) observed a maximum in the reaction rate which corresponded to a Cu(II) concentration

of 3 mol/L. Khandelwal et al. (1959) however, reported that increasing the Cu(II) concentration did not markedly increase the reaction rate.

Sondak and Dodge (1961a,b) studied the reaction in the presence of copper, iron, manganese, and vanadium and claimed no noticable effect of any of these metals on the reaction rate. On the other hand, iron complexes of cyanide in plating wastes were found resistant to ozonation by Mauk et al. (1976) and Streebin et al. (1981), who recommended coupling UV radiation with ozonation for complete destruction of iron–cyanide complexes.

This study was undertaken to understand the effects of complexation of cyanide with copper and iron on the kinetics and the mechanism of cyanide oxidation by ozone in aqueous solution. It was hoped that the findings would

help to resolve the apparent conflicts in the literature.

Experimental Methods

Ozone was contacted with cyanide solutions in a 500-mL glass reactor operated in semicontinuous fashion, i.e., continuous with respect to the gas flow and batch with respect to solution. The details of the experimental setup and the procedure were presented elsewhere (Gurol and Bremen, 1985).

The free-cyanide solutions were prepared by dissolving NaCN in a 0.01 M phosphate buffer. NaCN and CuCN were dissolved in the buffered solutions to obtain copper–cyanide complexes. Since the original ratio of CN/Cu was 4:1, $Cu(CN)_4^{3-}$ was the predominant species in solutions before ozonation (Rothbaum, 1957; Penneman and Jones, 1956). Solutions of iron–cyanide complexes were prepared by dissolving $K_3Fe(CN)_6$ in the buffered solutions. $Fe(CN)_6^{3-}$ was the predominant species in unozonated solutions (Busey, 1965; Broderius, 1973). The final pH of all the test solutions was adjusted to 11.5 to reduce the chance of HCN formation. NaOH was used for pH adjustments.

During the course of the ozonation of cyanide solutions, samples were taken at various time intervals. The samples were analyzed for total cyanide and cyanate concentrations. Cyanide ion in solutions of NaCN was measured by titration with $AgNO_3$ (*Standard Methods for the Examination of Water and Wastewater*, 1980) or by an Orion cyanide electrode. The solutions of copper–cyanide complexes were treated with EDTA under acidic conditions at 50 °C for decomplexation of cyanide (Frant et al., 1972). The concentration of cyanide was measured colorimetrically after it reacted with chloramine-T at neutral pH (*Standard Methods for the Examination of Water and Wastewater*, 1980). This technique yielded greater than 99% average recovery on 31 standard solutions.

The concentration of cyanide in solutions of iron complexes was measured by monitoring the light absorbance of $Fe(CN)_6^{3-}$ at 410 nm (Broderius, 1973). However, copper added to iron–cyanide solutions interfered with the absorption at this wavelength. Therefore, these solutions were exposed to UV radiation at acidic pH in the presence of sodium sulfide for decomplexation (Sekerka and Lechner, 1976). A Rayonet photochemical reactor equipped with 16 low-pressure mercury lamps, each emitting 1.5 W of 254-nm UV light, was operated for 30 min for each sample of 50 mL. After the addition of bismuth nitrate and pH adjustment to 11.5 (Sekerka and Lechner, 1976), cyanide ion was measured by the cyanide electrode. Acid distillation in the presence of $MgCl_2$, as described in *Standard Methods for the Examination of Water and Wastewater* (1980) for decomplexation of cyanides, was also tested for the copper and the iron complexes. However, this technique was not used routinely since it was time consuming, it required large sample sizes, and it did not produce significantly more accurate results than the EDTA and the UV decomplexation methods.

Cyanate ion in reaction mixtures was measured by acid hydrolysis (*Standard Methods for the Examination of Water and Wastewater*, 1980). The presence of copper or iron did not interfere with this procedure. An Ionics TOC instrument was used to measure the total organic carbon (TOC) and total carbon (TC) of selected samples.

Results and Discussion

Ozonation of Free and Copper-Complexed Cyanide. The solutions of free cyanide ion and the copper complexes of cyanide were ozonated at pH 11.5 under the same experimental conditions. The destruction of cyanide as a
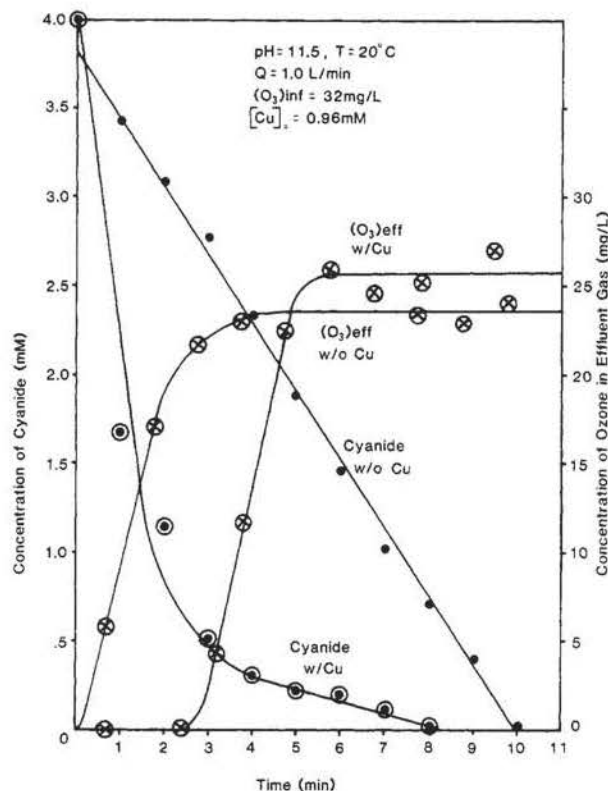

Figure 1. Oxidation of free cyanide and copper-complexed cyanide by ozone.

function of time of ozonation is depicted in Figure 1. No ozone could be detected in either solution, indicating the mass-transfer-limited nature of the process for both solutions. Gurol and Bremen (1985) studied the reaction between ozone and free cyanide by a stopped-flow spectrophotometer. The results indicated that the rate of the oxidation of free cyanide at pH 11.5 would be much faster than the absorption of ozone from the gas phase into the liquid phase.

The disappearance of free cyanide followed a straight line, as would be expected from a mass-transfer-limited process with constant mass-transfer coefficient (k_La) in a bubble contactor as follows (Gurol, 1985):

$$(rate)_{CN\ removal} = (rate\ of\ ozone\ absorption)/z \quad (1)$$

$$(rate\ of\ ozone\ absorption) = Q_g\{(O_3)_{in} - (O_3)_{eff}\} \quad (2)$$

$$(rate\ of\ ozone\ absorption) = Q_g(O_3)_{in}\{1 - e^{-\phi}\} \quad (3)$$

where z is the number of moles of ozone consumed per mole of cyanide oxidized, Q_g is the gas flow rate, $(O_3)_{in}$ and $(O_3)_{eff}$ are the concentrations of the ozone in the influent and the effluent gas streams, and

$$\phi = (k_La)V_L/HQ_g \quad (4)$$

Here k_La is the mass-transfer coefficient for ozone (gas-side mass-transfer resistance is negligible), V_L is the volume of water in the contactor, and H is the Henry's constant for ozone.

The oxidation rate of cyanide predicted by eq 1–4 agrees well with the observed rate shown in Figure 1 for the following experimental conditions: Q_g = 1.0 L/min, $(O_3)_{in}$ = 32 mg/L, $(O_3)_{eff}$ = 24 mg/L, V_L = 0.42 L, k_La = 100 h^{-1}. The values for H and z were measured earlier as 2.44 (Gurol and Singer, 1982) and 1 (Gurol and Bremen, 1985), respectively. These calculations indicated that the rate of mass transfer of ozone in the presence of cyanide was
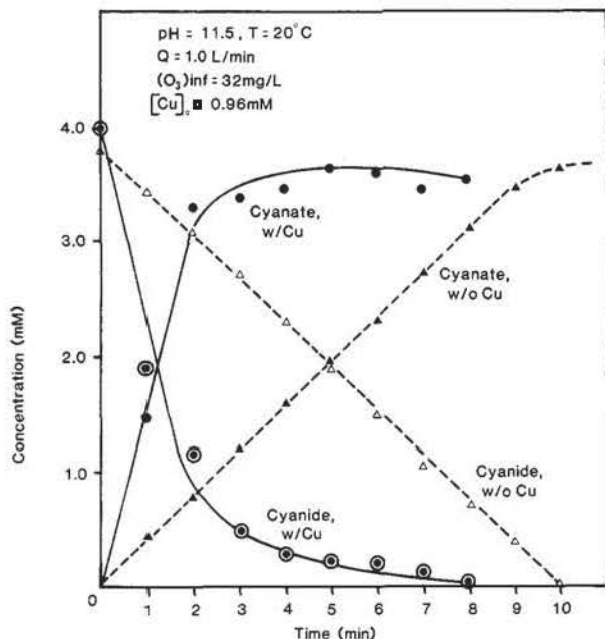
Figure 2. Oxidation of cyanide to cyanate by ozone.

Figure 3. Oxidation of cyanate by ozone.

not enhanced above its physical value, which was measured in the absence of the chemical reactions. Accordingly, the reaction regime prevalent during the oxidation of cyanide was an "intermediate reaction regime" (Danckwerts, 1970), and the reactions take place mainly in the bulk water.

The presence of copper increased the rate of cyanide disappearance significantly (Figure 1). Comparison of the initial rates indicates a 5-fold increase in the presence of copper under the experimental conditions. This increase in the rate of cyanide removal is due to an enhancement in the mass transfer of ozone, as is obvious in Figure 1. During the oxidation of free cyanide, ozone was detected in the effluent gas immediately, and its concentration reached a steady-state value of about 24 mg/L. However, during the oxidation of copper-complexed cyanide, no ozone was detected in the effluent gas for the first 3 min, indicating that all the ozone introduced to the solution was absorbed and reacted. The breakthrough occurred only after 85% of the cyanide was oxidized. Mass balance calculations revealed the consumption of 1 mol of ozone per mole of cyanide oxidized.

The enhancement in the rate of ozone absorption in the presence of copper can be caused by a physical effect of copper on the mass-transfer coefficient, such as an increase in the interfacial area "a" due to surface accumulation (Gurol and Nekouinaini, 1985). This possibility was checked by measuring the mass-transfer coefficient for oxygen in the presence and absence of copper in cyanide solutions under the same experimental conditions. The measurements were not significantly different from each other to justify the observed enhancement in ozone absorption in the presence of copper. Oxygen was used in these experiments because it does not react with cyanide or copper. These results and further evidence presented later in this paper indicate that the observed enhancement was more likely due to a change in the reaction regime from "intermediate" to "fast" because of the very fast reaction of ozone with copper.

During the oxidation of cyanide, copper released from cyanide complexes formed various precipitates in colors of blue, green, brown, and black. The reduction in the oxidation rate of cyanide after the third minute corresponded to the beginning of heavy precipitation, which
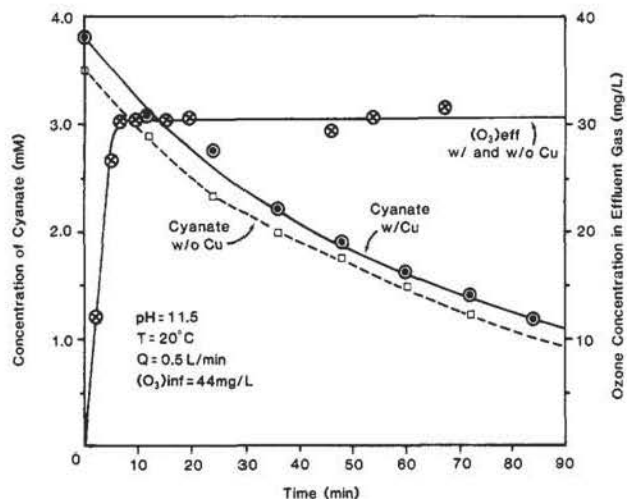
suggested that the decrease in the concentration of soluble copper and/or the change in the speciation might be responsible for the reduction in the reaction rate.

Cyanate. Cyanate, CNO^-, was produced as an intermediate product of the oxidation reaction, as shown in Figure 2. One mole of CNO^- was produced per mole of cyanide oxidized, in both the absence and presence of copper. It is believed that the oxidation of cyanide takes place according to a stepwise scheme which involves the formation of gaseous cyanogen, $(CN)_2$, as follows (Migrdichian, 1947; Williams, 1948; Deltombe and Pourbaix, 1955):

$$2CN^- \xrightarrow{\text{oxidation}} (CN)_2 \xrightarrow{OH^-} CN^- + CNO^- \quad (5)$$
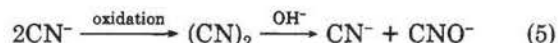
Cyanogen was also identified in this study in ozonated solutions of free and copper-complexed cyanide by directing the effluent gas from the reactor into a 0.5 M NaOH solution in which cyanogen gas was trapped. Cyanide which was produced upon hydrolysis of cyanogen according to the above reaction scheme was measured by the cyanide electrode. A KI trap was placed between the reactor and the NaOH solution to remove ozone from the effluent gas. Since cyanogen was measured only at trace levels (1–2 mg/L), and the rate of formation of cyanate was observed to be equal to the rate of oxidation of cyanide (Figure 2), the first reaction in the above reaction scheme is expected to be the slowest, and hence the rate-limiting step.

In the absence of ozone, the hydrolysis of cyanate to carbonate and ammonia, as suggested by Selm (1959), did not occur over a time period of 24 h. Nevertheless, cyanate was oxidized further by ozone. Balyanskii et al. (1972) reported for the reaction of ozone with cyanide and cyanate empirical and system-specific rate constants which combined the kinetics of mass transfer of ozone and of chemical reactions. On the basis of these rate constants, they concluded that cyanate is oxidized at one-fifth of the oxidation rate of cyanide. Bremen (1984) measured the true reaction rate constants by a stopped-flow spectrophotometer. The rate constant for the reaction of ozone with cyanate is reported to be 2 orders of magnitude smaller than the rate constant of cyanide oxidation. In Figure 2, cyanate was observed to accumulate until cyanide is oxidized completely; this is consistent with the 2 orders of magnitude difference in the reaction rate constants, as observed by Bremen.

The reaction of ozone with cyanate was studied by using the same experimental setup. The results of a typical
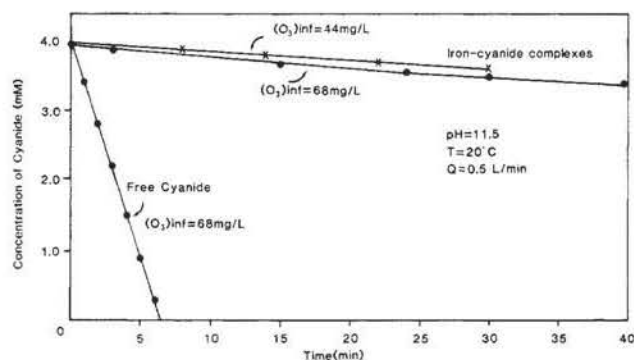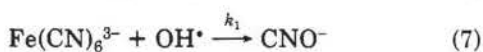
Figure 4. Oxidation of free cyanide and iron-complexed cyanide by ozone.

experiment are shown in Figure 3. No ozone was detected in the solution phase because of the accelerated self-decomposition of ozone at such high pH values. Under the experimental conditions, the absorption of a minimum of 5 mol of ozone was required for the oxidation of 1 mol of cyanate. This stoichiometric factor increased with ozonation time probably because of the competition presented by the reaction products for the oxidant. These observations support an indirect reaction mechanism in which the hydroxyl radicals generated upon decomposition of ozone, rather than molecular ozone, act as the predominant oxidizing agents (Hoigne and Bader, 1976). Contrary to the reports by Matsuda et al. (1975a,b), copper did not affect the rate of this indirect reaction (Figure 3). Ozone concentration in the effluent gas increased immediately to a value which remained stable throughout the experiment.

Ozonation of Iron-Complexed Cyanide. Figure 4 presents evidence that the complexation of cyanide to iron hinders the oxidation of cyanide by ozone to a great extent. This supports the earlier reports by Mauk et al. (1976) and Streebin et al. (1981).

Increasing the ozone concentration in the applied gas did not affect the oxidation rate of iron-complexed cyanide. After 90 min of ozonation, only about 25% of the cyanide was oxidized. Chemical analysis throughout this time period showed no buildup of cyanate in the solution. Independent experiments proved that iron did not interfere with cyanate analysis. Accordingly, the following explanation might be offered for the absence of cyanate in ozonated iron–cyanide complexes.

As in the case of cyanate, cyanide in $Fe(CN)_6^{3-}$ might be oxidized by the hydroxyl radicals which are produced upon self-decomposition of ozone. The observation of a requirement of more than 30 mol of ozone/mol of cyanide in iron complexes supports this statement. Hence, the reaction might take place according to the following scheme:

$$O_3 \xrightarrow{k_d} OH^\bullet \qquad (6)$$

$$Fe(CN)_6^{3-} + OH^\bullet \xrightarrow{k_1} CNO^- \qquad (7)$$

$$CNO^- + OH^\bullet \xrightarrow{k_2} \text{products} \qquad (8)$$

Comparison of Figures 3 and 4 leads to the conclusion that $k_2 > k_1$. Therefore, CNO^- is expected to react as soon as it is formed from cyanide. The rate constant k_1 might be determined by the relatively slow dissociation rate of Fe-$(CN)_6^{3-}$ complex into CN^-.

Solutions of $K_3Fe(CN)_6$ were ozonated in the presence of various amounts of copper (added as $CuSO_4$) to determine whether copper will also increase the rate of removal of cyanide which is in complexation with iron. The cyanide
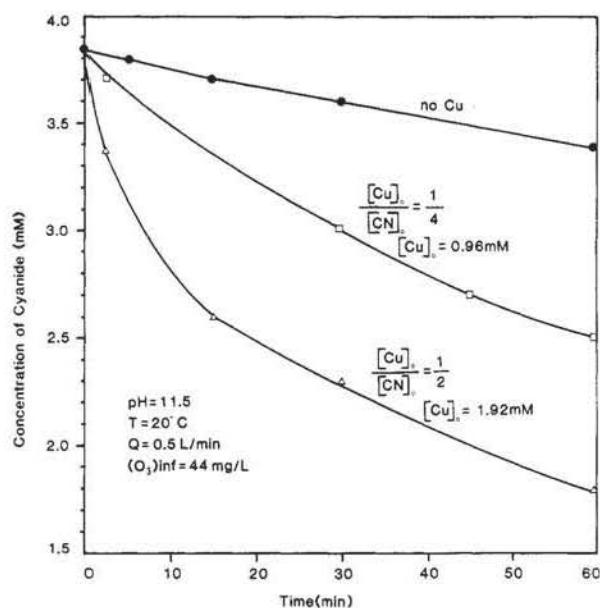

**Figure 5.** Effect of copper on the oxidation rate of iron–cyanide complex.

profiles for the Cu/CN ratios of 0, $^1/_4$, and $^1/_2$ are shown in Figure 5 for the same experimental conditions. The amount of cyanide which was removed from the solution during the first 15 min of ozonation increased by a factor of 4 in the presence of 0.96 mM copper and by a factor of 8 in the presence of 1.92 mM copper. The rate of removal reduced after the first 15 min, probably because of the precipitation of copper from the solution. During the reaction period, no buildup of cyanate was observed.

These experimental observations indicate that the iron–cyanide complexes in metal-plating wastewaters may not be oxidized by ozone within a reasonable period of time. However, in the presence of copper, e.g., copper-plating wastewaters, ozonation might still be an economically feasible treatment alternative.

The Mechanism of Copper Catalysis. Cu(II) is believed to be unstable in the presence of cyanide. According to Cotton and Wilkinson (1972), Cu(II) is reduced to Cu(I) as illustrated below:

$$4CN^- + 2Cu^{++} \rightarrow 2CuCN + (CN)_2 \qquad (9)$$

When coke plant wastewater was distilled in the presence of $CuCl_2$ for cyanide analysis, low results were observed by Barton et al. (1978). The authors believed that the oxidation of Cu(I) to Cu(II) by oxygen in air consequently caused the oxidation of cyanide as follows:

$$2Cu^{++} + 3CN^- + 2OH^- \rightarrow 2CuCN + CNO^- + H_2O \qquad (10)$$
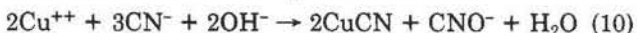
Bernardin (1973) observed the catalytic effect of Cu(I) on the oxidation of cyanide on granular activated carbon. Coleman (1968), who studied the oxidation of cyanide by Cr(VI), reported that the reaction occurred only in the presence of copper.

These observations suggest that the catalytic effect of copper on the oxidation of cyanide by ozone is due to an independent oxidation–reduction reaction between Cu(II) and cyanide. In order to test this hypothesis, Cu(II) as $CuSO_4$ was added in increments to cyanide solutions in various amounts at pH 11.5 in the absence of ozone. After 1 h of stirring at each concentration, the samples were analyzed for cyanide and cyanate. The results are summarized in Table I. Cu(II) oxidized free cyanide and cyanide in complexation with Cu(I), and cyanate was produced at approximately one-to-one ratio, as postulated

Table I. Oxidation of Cyanide by Copper (Concentrations in mM)

[Cu]/[CN]	free cyanide		copper–cyanide		iron–cyanide	
	cyanide remaining	cyanate produced	cyanide remaining	cyanate produced	cyanide remaining	cyanate produced
0	3.84	0	3.84	0	3.84	0
1/4	3.05	0.46	3.22	0.41	3.84	0
1/2	2.71	0.78	3.27	0.43	3.47	0
1/1	2.88	1.00	3.06	0.61	2.04	0
2/1	2.80	0.99	3.18	0.58	0.87	0

Table II. Carbon Balance on Ozonated Cyanide Solutions

components, mg/L of C	blank	free cyanide		copper–cyanide		iron–cyanide	
		I[a]	II[b]	I[a]	II[b]	I[a]	II[b]
TC	18	51	40	54	41	56	56
$TC-TC_{blank}$	0	33	22	36	23	38	38
TOC	<2	NM[c]	<2	NM	<2	NM	13
$TOC-TOC_{blank}$	0	NM	0	NM	0	NM	11
% CO_2 produced			67		64		71
% CN remaining			0		0		29
% CNO remaining			0		0		0
% C accountable			67		64		100

[a] I, before ozonation. [b] II, after prolonged ozonation. [c] NM, not measured.

above. Furthermore, cyanogen gas was identified in ozonated mixtures of copper–cyanide complexes, as mentioned earlier in this paper.

In view of the presented experimental evidence and that Cu(I) is expected to be oxidized to Cu(II) by ozone by a fast electron-transfer reaction, the following mechanism can be proposed to explain the effect of copper on the oxidation of cyanide ion by ozone:
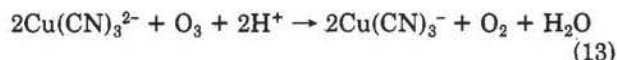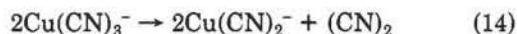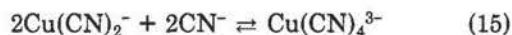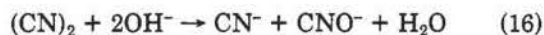
I

$$Cu^+ + 4CN^- \rightleftharpoons Cu(CN)_4{}^{3-} \qquad (11)$$

II

$$Cu(CN)_4{}^{3-} + O_3 \rightarrow Cu(CN)_3{}^{2-} + CNO^- + O_2 \quad (12)$$

III

$$2Cu(CN)_3{}^{2-} + O_3 + 2H^+ \rightarrow 2Cu(CN)_3{}^- + O_2 + H_2O \qquad (13)$$

IV

$$2Cu(CN)_3{}^- \rightarrow 2Cu(CN)_2{}^- + (CN)_2 \qquad (14)$$

V

$$2Cu(CN)_2{}^- + 2CN^- \rightleftharpoons Cu(CN)_4{}^{3-} \qquad (15)$$

VI

$$(CN)_2 + 2OH^- \rightarrow CN^- + CNO^- + H_2O \qquad (16)$$

net reaction:

$$2Cu^+ + 11CN^- + 3O_3 \rightarrow 2Cu(CN)_4{}^{3-} + 3CNO^- + 3O_2 \qquad (17)$$
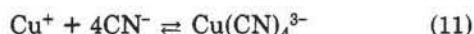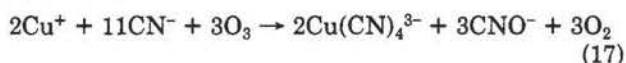
The second step in this reaction scheme represents the direct oxidation of cyanide to cyanate by ozone. In the third step, Cu(I) is oxidized to Cu(II). Cu(II) oxidizes cyanide to cyanogen (step IV), while it is reduced back to the Cu(I) form. An equilibrium is established quickly (step V). In the last step, cyanogen goes through a disproportionation reaction. Observations presented in Figures 3 and 4 are in complete agreement with the net reaction which indicates that the oxidation of 3 mol of cyanide in the presence of copper will require 3 mol of ozone and will produce 3 mol of cyanate. Two moles of copper enters an oxidation–reduction reaction which produces 1 mol of cyanate in addition to the 2 mol of cyanate produced from direct oxidation of ozone with cyanide.

The oxidation of Cu(I) to Cu(II) by ozone is expected to be much faster than the oxidation of cyanide by ozone, since the former is a direct electron-transfer reaction. Shambaugh (1976) estimated the rate constants of the ozonation reactions of metals like lead, nickel, zinc, etc., to the greater than 10^6 L/(mol·s), and he predicted that these reactions take place within the liquid film. The oxidation reaction of Cu(I) might similarly take place within the liquid film and enhance the ozone absorption. The observation of no ozone in the effluent in the presence of copper (Figure 1) is an indication that the reaction regime conforms with that of "fast" (Danckwerts, 1970). The enhancement factor is defined as the ratio of the mass-transfer rate in the absence of reaction to the rate in the presence of reaction at a dissolved gas concentration of zero. The enhancement factor is directly proportional to the concentration of the solute with which the gas reacts (Danckwerts, 1970). Hence, as the concentration of the copper is reduced in solution by precipitation, the enhancement factor is reduced in magnitude, causing a breakthrough in ozone in the gas effluent and subsequently a slow down in the removal rate of cyanide (Figure 1).

As shown in Table I, addition of $CuSO_4$ to iron–cyanide solutions also resulted in significant removals of soluble cyanide, although no cyanate formation was detected. The presence of neither iron nor copper had any observable interference on the analytical technique for cyanate. However, addition of copper to the solutions caused precipitation. The complexation of cyanide with iron is much stronger than with copper, i.e., $K_{eq} = 10^{47}$ for $Fe(CN)_6{}^{3-}$ (Broderius, 1973), $K_{eq} = 10^{30.3}$ for $Cu(CN)_4{}^{3-}$ (Penneman and Jones, 1956), and $K_{eq} = 10^{25}$ for $Cu(CN)_4{}^{2-}$ (Bjerrum, 1950). Therefore, the effect of copper on the oxidation rate of iron-complexed cyanide cannot be explained by an exchange mechanism between copper and iron. Additionally, the absence of cyanate in the reaction mixture indicates that the above mechanism is not applicable for iron–cyanide complexes. Hence, it is plausible to accept the formation of a precipitate of copper–iron–cyanide as the removal mechanism of soluble cyanide in iron–cyanide complexes.

Carbon Balance. Continued ozonation of cyanide resulted in the consecutive reaction of the primarily formed cyanate. Tyler et al. (1951) and Selm (1959) postulated that ozone reacts with cyanide to form carbonate and nitrogen gas. Balyanskii et al. (1972) measured about 70% conversion of cyanate into nitrate. The remaining 30%

was assumed to be oxidized to nitrogen.

In the present study, an attempt was made for a carbon balance after prolonged ozonation. The original and the ozonated solutions of free cyanide and copper and iron–cyanide complexes were analyzed by a TOC instrument for TC and for TOC after acid purging. The results are tabulated in Table II.

If the difference between the TC and the TOC values is assumed to be due to carbon dioxide, it can be concluded that about 65–70% of carbon in free cyanide and copper- and iron–cyanide complexes was converted into carbon dioxide which was captured as carbonate at high pH. Cyanide constituted the remaining 29% of carbon in the solution of iron–cyanide complexes. The unaccountable one-third of carbon in the solutions of free cyanide and copper–cyanide complexes might be attributable to volatile intermediate compounds, such as cyanogen gas.

Conclusions

The conclusions with regard to the effects of copper and iron on the kinetics and the mechanism of ozonation of cyanide can be summarized as follows: Oxidation of 1 mol of free cyanide requires 1 mol of ozone and produces 1 mol of cyanate. The reaction is faster than the rate of absorption of ozone into water under normal operating conditions of ozone reactors. The presence of copper causes a significant increase in the oxidation rate of cyanide. However, copper does not affect the stoichiometric relationships between cyanide, ozone, and cyanate. The mechanism of copper catalysis may involve an oxidation-reduction reaction between Cu(II) and cyanide ion and a change in the reaction regime due to the reaction of Cu(I) with ozone.

Cyanate is further oxidized by ozone. However, since the oxidation of cyanate is a slow reaction, cyanate accumulates in the solution until cyanide is oxidized completely. The oxidation rate of cyanate by ozone and the amount of carbon dioxide production are not affected by the presence of copper.

Complexation of cyanide with iron hinders the oxidation of cyanide significantly, as demonstrated earlier by Mauk et al. (1976) and Streebin et al. (1981). Cyanate is not detected as an intermediate product. Oxidation seems to be accomplished by the hydroxyl radicals which are generated upon decomposition of ozone. In the presence of iron, under the experimental conditions, more than 30 mol of ozone had to be absorbed into solution for the oxidation of 1 mol of cyanide.

Carbon dioxide (carbonate at pH 11.5) is the major end product of oxidation of free cyanide and the cyanide complexed to copper and iron.

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